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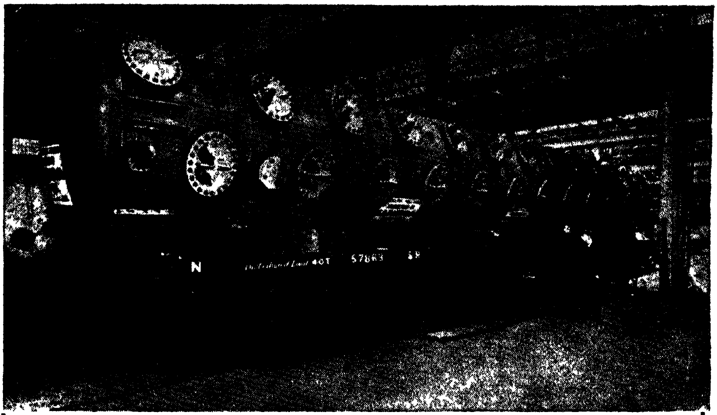

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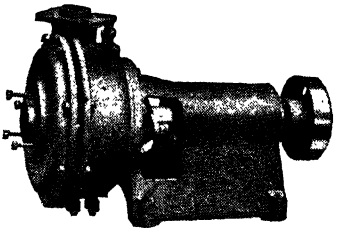

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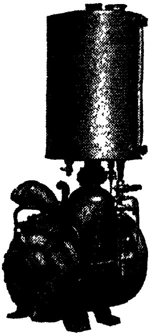

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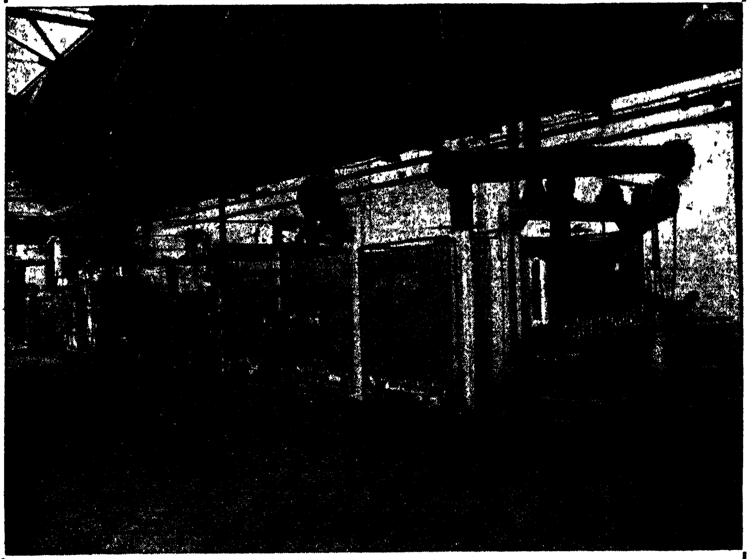

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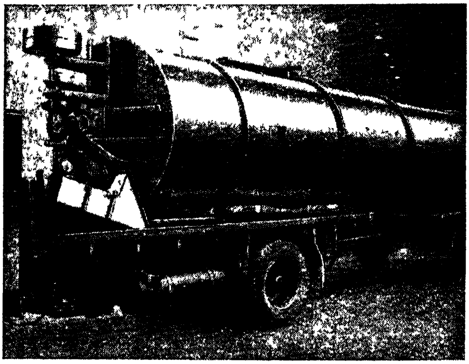

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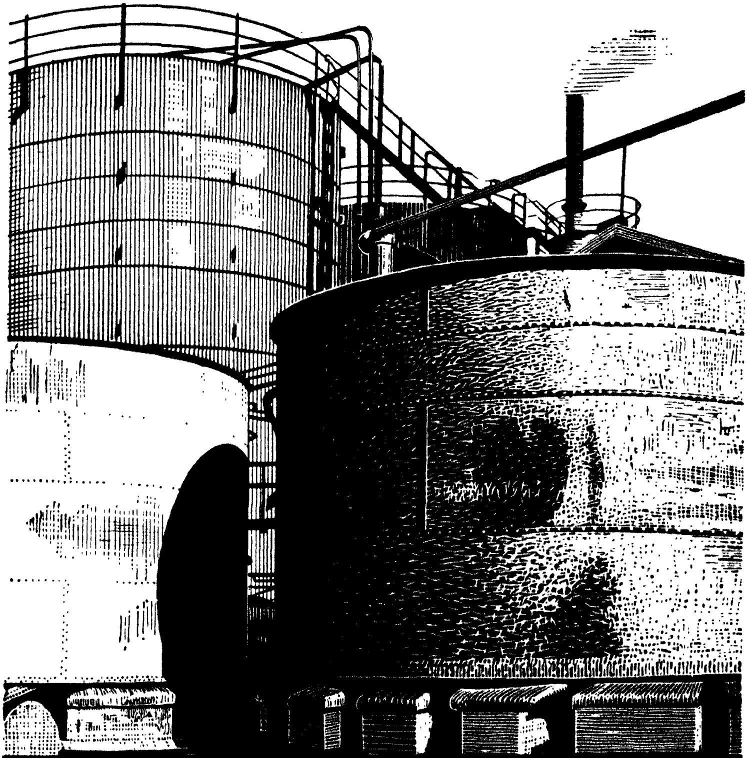

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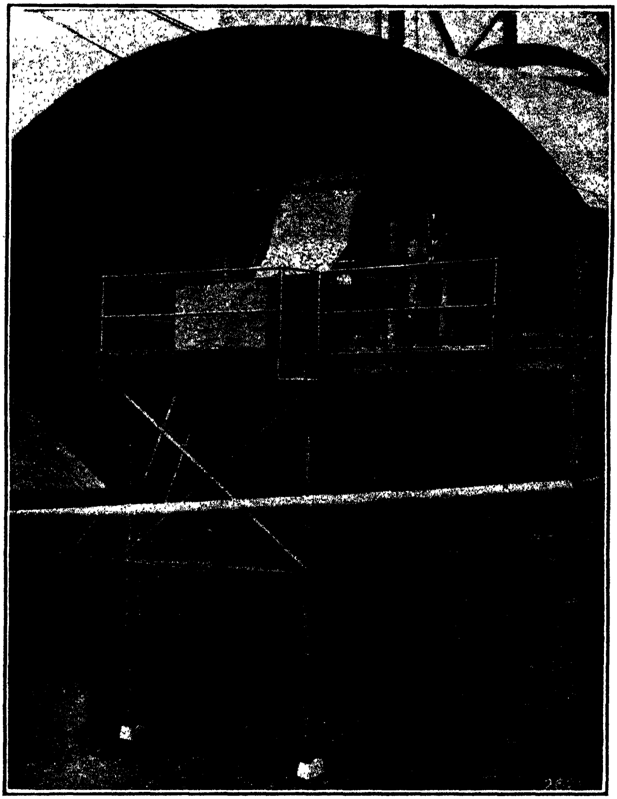

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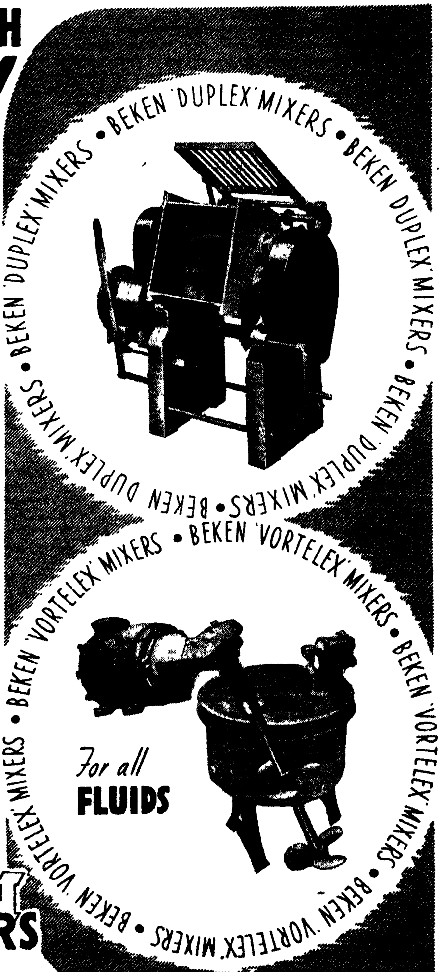
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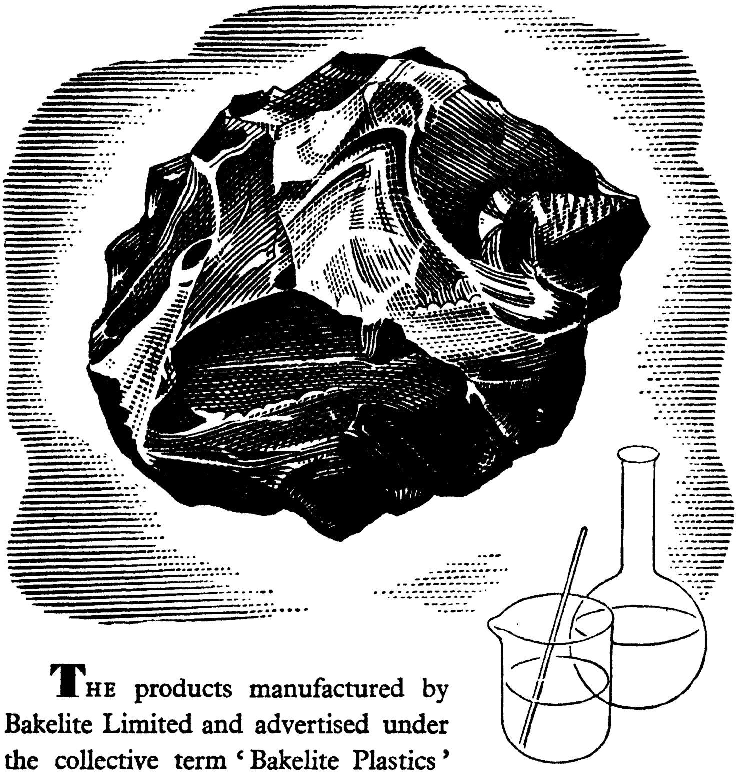

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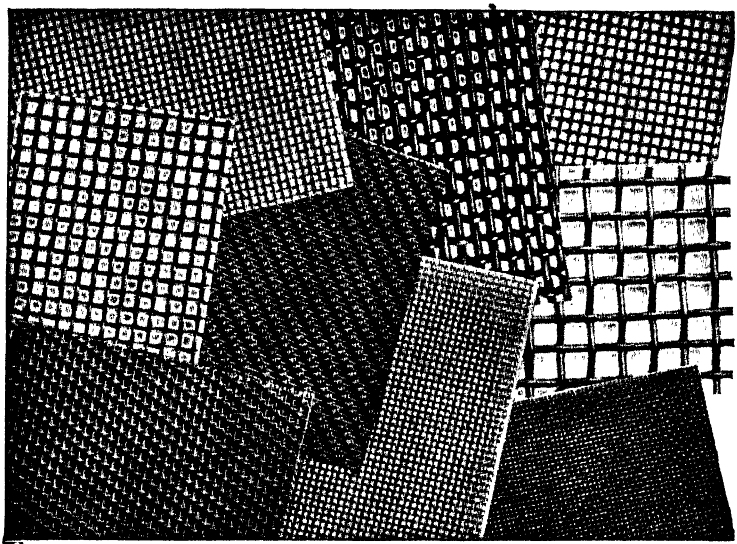

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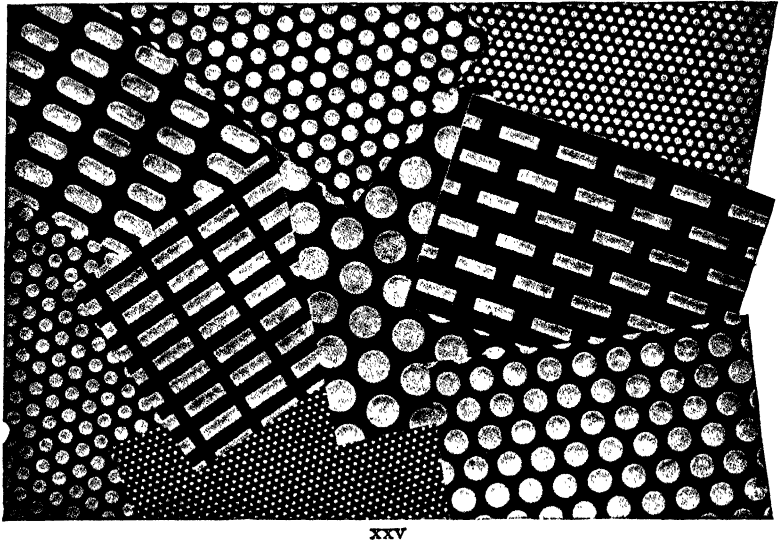

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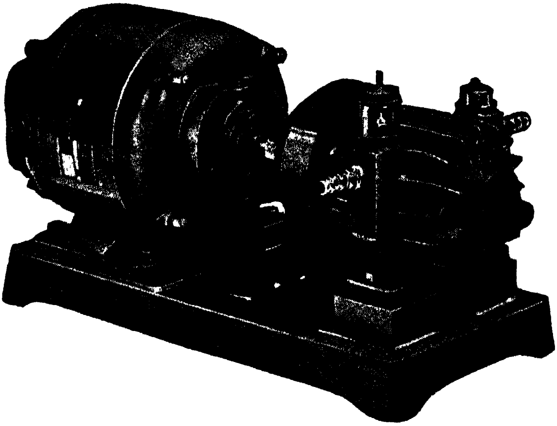

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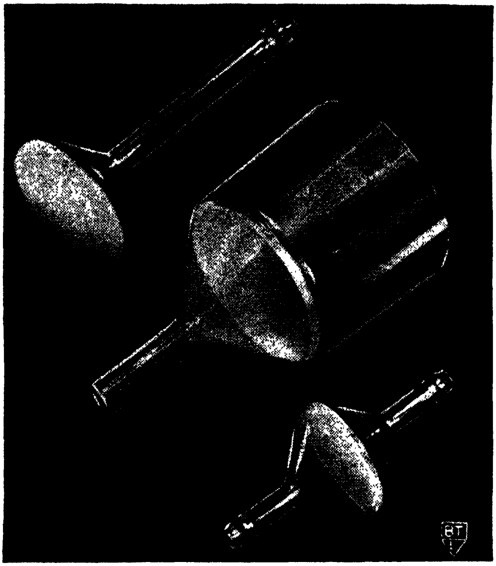

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Owing to paper shortage the Reports on Analytical Chemistry and Radio-activity and Sub-atomic Phenomena are being held over until next year.

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

1. INTRODUCTION.

THE nature of the Reports to follow has been altered to some considerable extent as compared with those of former years. In the past there has been a tendency to produce reviews which often were annual reports in the restricted sense of the term. Within the last few years an effort has, however, been made to render these reports of more general interest by confining the Reporter to one topic within the particular branch of physical chemistry being discussed. This year the process is being carried a stage further as a wartime experiment and expedient in the hope that these Reports will appeal to all interested in physical chemistry whilst retaining their authoritative and complete character.

The first report is concerned with the physicochemical behaviour of rubber solutions. From the thermodynamic point of view it is of great interest to know something about the behaviour of solutions of high-molecular substances because of their unusual properties; but simultaneously that knowledge proves to be extremely useful in learning a good deal about the structure of the rubber molecule itself.

In the next section there is an account of the reactions of sodium atoms with a variety of organic and inorganic halides. These reactions have in general a low activation energy and their study has only been made possible by the extensive development of the technique of the so-called dilute "flames."

Finally, the interesting developments in the physical chemistry of the formation of the photographic latent image are recorded. In spite of much effort it is only recently that some reliable insight has been gained into the precise nature of the reaction of radiation with photographic emulsions and the manifold resultant effects that have been noted almost since the beginning of photography. H. W. M.

2. THE PHYSICAL CHEMISTRY OF RUBBER SOLUTIONS.

THE physicochemical behaviour of rubber may conveniently be described in terms of two main factors, (1) its long-chain character, and (2) its chemical nature. It is frequently possible to neglect one of these; *e.g.*, E. H. Farmer *et al.*,[1] have shown that much light can be thrown on the organic chemistry of rubber from a study of structurally related, low-molecular hydrocarbons. In the following we shall, in the main, consider rubber as a typical member of the class of long-chain compounds, and much of this section is therefore of general application to linear high polymers.

The Micellar Theory of Rubber Structure.

In view of this line of approach, it is natural to consider first the evidence for the size and shape of the rubber molecule. Two main points of view have been expressed. According to the first,[2] rubber consists of molecules having a molecular weight of *ca.* 1000—1500, which in solid rubber are united in the form of "micelles." These larger units are supposed to have sufficient individuality to resist dispersion by most solvents, so that, *e.g.*, the osmotic pressure of a benzene solution measures the size, not of the molecule, but of the micelle. Only such solvents as camphor, menthol, and related materials are considered to break down the rubber to give a molecular dispersion. The alternative view [3] regards rubber as truly macromolecular, *i.e.*, made up of very long chains of isoprene molecules, polymerised into single molecules whose size, measured osmotically, is of the order of 100,000. A recent critical examination [4] seems to disprove the whole of the evidence advanced in support of the former view. The results of the earlier workers were shown to arise primarily from the rapid oxidative breakdown of rubber in molten camphor. When this is prevented by the exclusion of air, camphor behaves very similarly to benzene as a rubber solvent. The abnormally low molecular weights reported were obtained by the Rast method and are now shown to be merely indicative of the "non-ideal" behaviour which is characteristic of rubber solutions in general (see below). In default of any sound evidence for the micellar theory, we therefore conclude that rubber is to be classed with the synthetic polymers as a macromolecule.

Osmotic Pressure Measurements.

The molecular weight of rubber may be determined by three methods : (*a*) ultracentrifugal, (*b*) osmotic, and (*c*) viscosimetric. Of these, (*c*) is not an absolute method, and (*a*) has been applied to a very limited extent, so that we must of necessity rely mainly on (*b*). Osmotic-pressure measurements of rubber solutions have been reported by a series of workers,[5] whose results show considerable deviations in detail, but with general agreement in finding molecular weights of the order of 1—4 × 10^5. The calculation of molecular weight from osmotic data is by no means straightforward, since the usual relationship between them is found not to hold. According to van't Hoff's law, the osmotic pressure Π is related to the molecular weight M of the solute and its concentration c by the equation

---

[1] *J.*, 1942, 121; *Trans. Faraday Soc.*, 1942, **38**, 340.

[2] R. Pummerer *et al.*, *Ber.*, 1927, **60**, 2167; 1929, **62**, 2628; *Kautschuk*, 1929, **5**, 129.

[3] H. A. Staudinger, "Die Hochpolymeren Organischen Verbindungen" (Julius Springer, 1932).

[4] G. Gee, *Trans. Faraday Soc.*, 1942, **38**, 109.

[5] Reviewed by H. Staudinger and K. Fischer, *J. pr. Chem.*, 1941, **157**, 19; cf. also refs. (19) and (29).

$$\Pi = c\boldsymbol{RT}/M \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Experimentally it is found that Π/c is a function of c and the equation has therefore been used in the form

$$M = \boldsymbol{RT} \lim_{c \to 0} (c/\Pi) \quad . \; . \; . \; . \; . \; . \quad (2)$$

Two difficulties are raised by this procedure : the experimental one of performing the extrapolation satisfactorily, and the need for some explanation of the departure from the simple law before any confidence can be placed in the results.

Wo. Ostwald [6] showed that the osmotic pressures of polymer solutions could be represented satisfactorily by an equation of the form

$$\Pi = ac + bc^n \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where a, b, and n are constants. He identified a with $\boldsymbol{RT}/M$, which is equivalent to assuming equation (2), and considered the first term as the true osmotic pressure. The second term, bc^n, in which n lay between 2 and 3, was regarded as a " swelling pressure," by analogy with the work of E. Posnjak,[7] who had shown that if a piece of rubber was confined by a piston in a cylinder whose base, permeable to solvent, was immersed in solvent, the degree of swelling of the rubber was determined by the pressure applied to the piston. The pressure P corresponding to a given concentration c of rubber in the swollen mass was represented by an equation of the form

$$P = bc^n \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where the constants b and n were characteristic of the liquid, n lying usually between 2 and 3. Ostwald regarded the pressure measured by an osmometer as composite of an osmotic pressure and a swelling pressure. Although it will be shown later that this explanation must be rejected, equation (3) has been widely used, especially by S. R. Carter and B. R. Record [8] and by K. H. Meyer and his co-workers.[9] The latter take $n = 2$, so that Π/c becomes a linear function of c.

An alternative explanation of the osmotic anomaly was proposed by O. Sackur [10] and applied to rubber by K. H. Meyer and H. Mark.[11] The dissolved particles were assumed to be solvated, so that the effective concentration of the solution was increased. Sackur took the volume of solvent removed in this way per g. of solute, to be independent of the solute concentration and wrote, instead of equation (1) :

$$\Pi = [c/(1 - cs)]\boldsymbol{RT}/M \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

---

[6] *Kolloid-Z.*, 1929, **49**, 60.

[7] *Kolloid-Beih.*, 1912, **3**, 417.

[8] *J.*, 1939, 660.

[9] *Helv. Chim. Acta*, 1940, **23**, 488.

[10] *Z. physikal. Chem.*, 1910, **70**, 477.

[11] *Ber.*, 1928, **61**, 1947.

where s was a constant. G. V. Schulz[12] has further modified this equation by representing s as a function of Π by the equation

$$\Pi s^{\nu} = k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which is again based on Posnjak's swelling-pressure equation (4). Combination of (6) with (5) leads to

$$M = c\boldsymbol{RT}/\Pi\{1 - c(k/\Pi)^{1/\nu}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation has been employed very extensively by Schulz and has been applied to rubber by Staudinger and Fischer.[5] It use in extrapolating osmotic data requires the evaluation of the constants k and ν, which is done by the authors by a series of approximations. Where measurements are available for a series of M values, each Π/c–c curve is extrapolated roughly, and the resulting M inserted in equation (5) to calculate s. The extrapolations are then adjusted until all the s values obey an equation of the form (6). A more direct method suggested by G. Gee[13] is to plot Π/c against $\sqrt{\Pi}$, which will be nearly linear if ν has the expected value of *ca.* 2. The degree of solvation required by this theory is very large (*ca.* 60 c.c. per g. of rubber in a 1% solution of rubber in benzene[14]) and cannot be held by any "chemical" bond. Even if we could regard this solvent as mechanically held by a sponge-like molecule, equation (6) cannot hold down to infinite dilution, for at this point $s \longrightarrow \infty$. Both as a method of extrapolation and as an explanation of the osmotic behaviour of solutions, this treatment must be regarded as thoroughly unsatisfactory.

An entirely different line of approach was suggested by R. E. Powell, C. R. Clark, and H. Eyring.[15] Pointing out that in many of its properties solid rubber behaves as though its molecules were composed of a large number of relatively short "segments," capable of more or less independent action, these authors apply the same idea to rubber solutions. Van't Hoff's law is assumed to hold provided we use, in place of the actual number of rubber molecules present n_r, the "effective" number n_r^*. These are related to the volume fraction v_r of rubber in the solution and the molecular weight M_s of the segments of solid rubber by the empirical equation :

$$n_r^* = n_r[1 + (M/M_s - 1)v_r] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The Reporter can see no justification for the assumptions involved in writing this equation. By use of approximations valid for dilute solutions this leads to

$$\Pi = \boldsymbol{RT}c/M + \boldsymbol{RT}c^2/\rho_r M_s \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where ρ_r is the density of the rubber. This is evidently of the same form as (3), and has been employed by the authors to calculate values of M_s from the slope of the Π/c–c curve. Results obtained vary between 900 and 4500, and are considerably larger than the segment sizes deduced in other ways.

---

[12] *Z. physikal. Chem.*, 1936, *A*, **176**, 317. [13] *Trans. Faraday Soc.*, 1940, **36**, 1162.

[14] Calculated from the data of Gee and Treloar, ref. (19).

[15] *J. Chem. Physics*, 1941, **9**, 268.

Although this paper is of value in emphasising that the rubber molecule may not be the effective unit in solution, we shall see later that a much more satisfactory explanation can be given of the varying slopes of the Π/c–c curves obtained in different solvents. [If (9) were valid these should, of course, all be equal.]

Before these theories can be further appraised, it is desirable to examine both the nature of osmotic pressure and the assumptions involved in the derivation of van't Hoff's equation. In considering the nature of the osmotic pressure of rubber solutions, it is necessary to abandon the kinetic picture frequently advanced of a pressure produced by the solute molecules bombarding the membrane. E. Guggenheim [16] has pointed out some of the difficulties associated with this view, and they are further enhanced if we compare the osmotic pressure of a rubber solution with the swelling pressure of a rubber gel. Thermodynamically, these can both be defined as the hydrostatic pressure which has to be applied to the solution (or gel) in order to increase the vapour pressure of the solvent in the solution until it becomes equal to that of the pure solvent. Under these conditions the solution (or gel) is in osmotic equilibrium with the solvent, and it is obvious that osmotic pressure and swelling pressure are actually synonymous terms. Both are, in fact, to be understood, not as pressures exerted by the solute, but as pressures applied by the observer. Their physical origin may be regarded as the tendency of solvent molecules to flow from solvent to solution because of the increase of entropy which results. It can be shown that,[17] for an ideal solution

$$\Pi V_0 = T\Delta S_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where ΔS_0 = entropy of dilution and V_0 = molar volume of liquid.

In applying a pressure to the solution we compress it slightly, reducing the mean intermolecular spacing, and producing (*a*) a decrease of entropy and (*b*) an increase of the energy content of the liquid. These factors combine to oppose the increase of entropy tending to cause osmosis, and at a certain pressure, osmotic equilibrium results. If α is the coefficient of thermal expansion of the liquid at constant pressure it may be shown [18] that the decrease of entropy is given by $\alpha V_0 P$ and the increase of energy by $V_0 P(1 - \alpha T)$. Since $\alpha \simeq 10^{-3}$ for organic liquids, the second term is generally the more important. This way of considering the problem emphasises the fallacy involved in comparing a solution with a perfect gas, for which $\alpha = 1/T$, and the effect of pressure is solely to decrease the entropy. The increase of vapour pressure with applied hydrostatic pressure is also readily understood on this basis. It is easy to derive from it the thermodynamic relationship [19] between osmotic pressure and the vapour pressures of the solvent (p_0^o) and solution (p_0^m) :

$$\Pi V_0 = RT \ln p_0^o/p_0^m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

---

[16] "Modern Thermodynamics," Methuen, 1933, pp. 85 *et seq.*

[17] E. Guggenheim, *op. cit.*, p. 97; cf. ref. (20).

[18] G. N. Lewis and M. Randall, "Thermodynamics," 1923, p. 133 (McGraw Hill).

[19] G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, 1942, **38**, 147.

The theoretical basis of van't Hoff's law may be given in several ways: (1) The kinetic interpretation of osmotic pressure leads to it by analogy with gas pressure; rejection of this interpretation necessarily invalidates this line of argument. (2) If we assume Raoult's law to hold, we may replace $p_0{}^m/p_0{}^o$ in equation (11) by N_0, the mol.-fraction of solvent in the solution; for dilute solutions, the expansion $\ln N_0 \simeq 1 - N_0$ leads readily to van't Hoff's equation—this method merely exchanges one assumption for another which is in equal need of justification. (3) If the molecules of solvent and solute are regarded as approximately equal spheres, it can be shown statistically [20] that the entropy of dilution is given by $\Delta S_0 = -\boldsymbol{R} \ln N_0$, which on substitution into equation (10) gives the same result as above. This gives us a molecular basis for the law, and reveals at once the cause of its failure to apply to rubber solutions, for it is evident that the rubber molecule is *not* to be regarded as equal in size to the solvent molecule. The interpretation of the osmotic behaviour of rubber solutions thus reduces to the statistical calculation of the entropy of dilution. K. H. Meyer [21] pointed out that this might be done approximately by computing the number of ways of arranging a long flexible chain on an array of lattice points. Each point may be occupied either by a solvent molecule or by a "segment" of the rubber chain, approximately equal in volume to the solvent molecule. The number of configurations possible is, of course, restricted by the fact that successive segments must occupy adjacent lattice points. Meyer's suggestion was worked out independently by P. J. Flory [22] and M. L. Huggins,[23] the entropy of mixing being calculated from the probability at a given concentration by means of Boltzmann's equation. Flory's result was:

$$\Delta S_0 = -(\boldsymbol{R}/\beta)[\ln v_0 + (1 - 1/x)v_r] \quad . \quad . \quad . \quad (12)$$

where x is the number of segments in the rubber molecule; v_0 and v_r are the volume fractions of solvent and rubber; and β is the number of solvent molecules which are replaceable by one segment.

Both Meyer's original statement and Huggins's treatment assume $\beta = 1$. The latter's analysis leads to a similar result:

$$\Delta S_0 = -\boldsymbol{R}[\ln v_0 + g_0(1 - 1/x)v_r] \quad . \quad . \quad . \quad . \quad (13)$$

where

$$g_0 = 1 + \sum_{i=1}^{\infty} \frac{1}{i}\left(\frac{2v_r}{Z'}\right)^{i-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and Z' is very nearly equal to the co-ordination number Z of the lattice. Direct calculation of the number of configurations is difficult for long-chain molecules, and an alternative method of approach has been used by A. R.

---

[20] R. H. Fowler and E. Guggenheim, "Statistical Thermodynamics," 1939, p. 163 (Camb. Univ. Press).

[21] *Helv. Chim. Acta*, 1940, **23**, 1063.

[22] *J. Chem. Physics*, 1941, **9**, 660; 1942, **10**, 51.

[23] *Ibid.*, 1941, **9**, 440; *Ann. N.Y. Acad. Sci.*, 1942, **43**, 1; *J. Physical Chem.*, 1942, **46**, 1; *J. Amer. Chem. Soc.*, 1942, **64**, 1712.

Miller.[24] Improving on earlier analyses,[25] he applied the Bethe approximation to evaluate the entropy of mixing of solvent molecules with " polymers " which could be regarded as made up of two or three units similar in size to the solvent. By a consideration of the way in which the results depended on the number of units it was possible to extrapolate to very long chains. Miller's final result [26] is

$$\Delta S_0 = -\boldsymbol{R}\left[\ln v_0 - \frac{Z}{2}\ln\left\{1 - \frac{2v_r}{Z}\left(1 - \frac{1}{x}\right)\right\}\right] \quad . \quad . \quad (15)$$

In the concentration range in which osmotic methods are applied, all three analyses lead to an equation of the form :

$$\Pi/c = \boldsymbol{R}T/M + kc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

k being given by $\boldsymbol{R}T/2\beta\rho_r{}^2V_0$ (Flory and Huggins) or $\boldsymbol{R}T(1/2 - 1/z)/\rho_r{}^2V_0$ (Miller) where ρ_r is the density of the rubber. It is probable that these calculations of entropy can be refined, but even in their present state they provide a perfectly natural explanation for the departure of rubber solutions from van't Hoff's law. It is now clear that this law could not be expected to hold even in solutions in which the heat of dilution ΔH_0 is zero. When the heat of dilution is not zero, a further complication arises, for we have then [19]

$$\Pi V_0 = T\Delta S_0 - \Delta H_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Few measurements have been made of the heat of dilution of rubber solutions, and none of sufficient accuracy to determine the form of the relationship between ΔH_0 and c. There is no reason, however, to expect this to differ from that found for mixtures of two liquids. J. H. Hildebrand [27] has shown that in the latter case ΔH_0 may be expressed as a power series in v_r, in which the first term involves $v_r{}^2$. Now, for dilute solutions $c \propto v_r$ and we may write

$$\Delta H_0 = k_2c^2 + k_3c^3 + \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Combination of (16) and (18) gives for the reduced osmotic pressure

$$\Pi/c = \boldsymbol{R}T/M + (k - k_2)c - k_3c^2 \quad . \quad . \quad . \quad . \quad (19)$$

This equation will be seen to afford a justification for the use of equation (2) for the calculation of molecular weights from osmotic data. It is important to notice that if the expression for ΔH_0 (18) had contained a term k_1c, the extrapolated value of Π/c would have been $\boldsymbol{R}T/N - k_1$, which of course does not permit the use of equation (2). Evidence in favour of the assumption $k_1 = 0$ is derived (1) from measured heats of mixing of simple liquids, and (2) from the fact that $\lim\limits_{c \to 0} (\Pi/c)$ for polymers is independent of the nature of the solvent, in the few cases for which data are available.[28]

The initial slope of the Π/c–c curve is given by (19) as $k - k_2$, where k_2

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[24] *Proc. Camb. Phil. Soc.*, 1942, **38**, 109.

[25] T. S. Chang, *Proc. Roy. Soc.*, 1939, *A*, **169**, 512.

[26] *Proc. Camb. Phil. Soc.* (in press).

[27] " Solubility," Reinhold (1936).

[28] The best examples are given by (Mme.) A. Dobry's data, *J. Chim. physique*, 1935, **32**, 50; *Kolloid-Z.*, 1937, **81**, 190.

depends on the nature of the solvent. The slope therefore depends on the solvent, and it is evident that if a solvent can be found such that $k_2 = k$, it will form solutions which obey van't Hoff's law. Such solutions are, however, properly regarded as being *less* and not *more* " ideal " than those in which $k_2 = 0$.

We are now in a position to discuss the evaluation of molecular weights from the published osmotic data, and it is evident that the problem is essentially that of finding the best method of extrapolation. The difficulty becomes acute for high-molecular rubbers, since different methods of extrapolation, all equally consistent with the data, may lead to molecular weights differing by a factor of 2 or more.[13] Attempts to improve the extrapolation by measurements at higher dilution are of doubtful value on account of the increasing experimental error. The theoretical considerations given above support the method suggested by Meyer [9] of a linear extrapolation of Π/c–c. On the other hand, the most careful experimental work seems to be definitely opposed to this simple view. Gee and Treloar,[19] by means of osmotic- and vapour-pressure data, have covered the whole range of concentration for the system rubber–benzene, and find a continuous curvature of the Π/c–c plot. A set of points covering a limited concentration range might, it is true, be considered collinear within experimental error, but both the slope and the extrapolated value depend on the particular set of points chosen. It does not, in fact, appear possible to find with certainty the limiting value of $(\Pi/c)_{c=0}$ from these measurements alone, at any rate in the case of the highest molecular-weight rubbers. A method of avoiding this difficulty was suggested by Gee.[29] By using a mixture of solvent and non-solvent it is possible to increase ΔH_0 until the osmotic behaviour of the solution approximates to van't Hoff's law *at one temperature*. For instance, rubber solutions in benzene + 15% methyl alcohol at 25° give values of Π/c almost independent of c from 8 to 20 g./l. This value of Π/c is considered to give the best available estimate of RT/M, and is consistent with the general curvature of the Π/c–c curves for rubber in benzene. A series of rubbers of different molecular weights were studied by Gee and Treloar, and their Π/c–c curves in benzene form a band whose width diminishes with increasing concentration, until at a concentration of *ca.* 80 g./l. the effect of molecular weight is indetectable. In Fig. 1 the curves for the highest and lowest members of the series are plotted, together with some older data obtained by earlier workers.[11, 30, 31] The curves have been drawn through the latter points in such a way as to fit them into the general results of Gee and Treloar. Although the curves are consistent with the data, it is obvious that they are not derivable from the data alone. A similar family of curves for toluene solutions of rubber has been constructed by combining the data of K. H. Meyer and C. G. Boissonnas [32] with those of Staudinger and Fischer [5]

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[29] *Trans. Faraday Soc.*, 1940, **36**, 1171; 1942, **38**, 108.
[30] W. A. Caspari, *J.*, 1914, **105**, 2139.
[31] H. Kroepelin and W. Brumshagen, *Ber.*, 1928, **61**, 2441.
[32] *Helv. Chim. Acta*, 1940, **23**, 430.

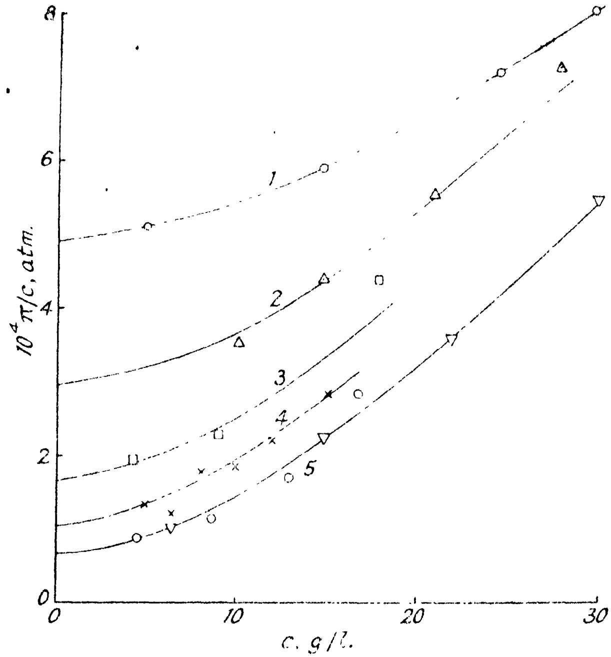

FIG. 1.

Osmotic Pressure of Rubber in Benzene.

Curve.	Symbol.	Material.	Ref.
1	⊙	Thermally degraded rubber A	19
2	△	Fresh rubber	30
3	⊡	Crepe, alkali-treated	11
4	×	Ether sol	31
5	▽	Intermediate latex fraction	19
5	⊙	Crepe	

and is shown in Fig. 2. Considered as a whole, Fig. 2 is probably the best representation of the data, especially if the more complete results for benzene are taken as a guide. On the other hand, other extrapolations of any individual set of measurements are evidently possible. In Table I the

TABLE I.

				$10^{-5}M$.	
Type of Rubber.	Solvent.	Ref.	Extra-polation.*	Authors' value.	Figs. 1 and 2.
Raw crepe	PhH	11	1	3·6	*ca.*3
Crepe, alkali treated	,,	11	1	1·5	1·5
Ether sol rubber	,,	31	1	1·9	2·3
"Fresh" rubber	,,	30	2	1·3 †	0·8
Lightly milled crepe	PhMe	32	3	2·7	1·5
Rubber purified with Al_2O_3	,,	5	4	3·5	3·5
Sol rubber	,,	5	4	$2{\cdot}4_5$	$1{\cdot}8_5$
Rubber purified by Pummerer's method	,,	5	4	1·10	0·90

* Methods of extrapolation were: (1) Sackur's equation, (2) Ostwald's equation, (3) Ostwald's equation with $n = 2$, (4) Schulz's equation.

† Calculated by Ostwald.[6]

molecular weights obtained from Figs. 1 and 2 are compared with those calculated by the actual experimenters, whose methods of extrapolation are also recorded.

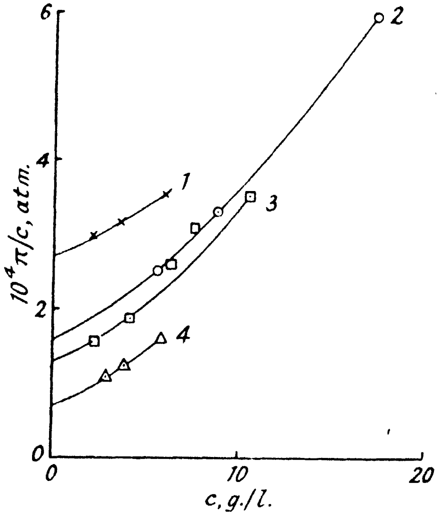

FIG. 2.

Osmotic Pressure of Rubber in Toluene.

Curve.	Symbol.	Material.	Ref.
1	×	Purified rubber	5
2	⊙	Lightly milled crepe	32
3	⊡	Sol rubber	5
4	△	Al_2O_3-purified rubber	5

This review of the situation suggests that most of the published osmotic molecular weights of rubber may be subject to considerable uncertainty. The Reporter's opinion is that the above method of interpreting the data leads to the most probable molecular weights from existing data, and that, for future measurements, the best method is to find a solvent in which Π/c is independent of c over the working range. For rubber such a solvent is benzene + 15% of methyl alcohol. It should be pointed out that this opinion is contrary to the views of other workers, of whom probably a majority favour linear extrapolation of Π/c–c.[33]

If the Π/c–c plot is truly non-linear, it appears to suggest that the calculated entropy of dilution is not quite accurate. Before we can be sure of this, it is necessary to have accurate data for the heat of dilution, and these are lacking. Several attempts have been made to estimate ΔH_0 from the temperature coefficient of osmotic pressure, but it has not hitherto been possible to obtain accurate data in this way. Meyer and Boissonnas[32] give data for toluene solutions which are consistent with the expression $\Delta H_0 = 20v_r^2$ cals./mol., but the probable experimental error is ± 50% and the form of the equation is obviously indeterminate. Gee and Treloar [19] give for benzene solutions $\Delta H_0 = 55v_r^2$ with a probable error of $\pm 30\%$. Earlier data of Kroepelin [34] lead to much larger heats, but are of extremely doubtful accuracy. All these workers agree in finding positive values of ΔH_0, and this is confirmed by direct calorimetric measurements of the integral heat of swelling.[35] The precise value found in this way depends somewhat on the history of the rubber sample, and is difficult to measure with precision, but values of the order of 2 cals./g. of rubber were found in the case of benzene, with a smaller value (*ca.* 0·5 cal./g. of rubber) for toluene. Chlorinated solvents gave an evolution of heat ($CHCl_3$, 3 cals./g.; CCl_4, 2 cals./g.). The only data covering a wide concentration range are those of Gee and Treloar [19] for benzene, calculated from vapour-pressure data. The accuracy is limited both by the smallness of the effect and by the relatively large correction for the non-ideal behaviour of benzene vapour.[36] The data are not satisfactorily represented by the simple quadratic equation, and a modified form was suggested, *viz.*, $\Delta H_0 = 156v_r^2/(1{\cdot}7 - 0{\cdot}7v_r)^2$. An alternative, based on (18), would be $\Delta H_0 = 55v_r^2 + 100v_r^3$. In Fig. 3 the entropy of dilution for the rubber–benzene system is compared with the theoretical results of Flory and Miller, calculated from equations (12) and (15). In each case one arbitrary constant has to be evaluated, and values of $\beta = 1, Z = 6$ have been selected in the following way :

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[33] Mark accepts this as a fact in his book " Physical Chemistry of High Polymers " (Interscience Publishers, 1940).

For sufficiently small values of v_0, equation (12) gives $\Delta S_0 \longrightarrow -(\boldsymbol{R}/\beta)\ln v_0$. Now, in this region, the vapour pressure is given [19] by $p_0^m/p_0^o = \alpha v_0$, where $\alpha = 4{\cdot}4$ at 25°. This result requires that the limiting value of ΔS_0 shall be $-\boldsymbol{R}\ln v_0$, whence $\beta = 1$. A better fit over the main part of the curve results from taking $\beta = 1{\cdot}3$, but a complete fit would require β to be made an empirical function of v_0. Miller's equation (15) gives $\Delta S_0 \longrightarrow -\boldsymbol{R}\ln v_0$ for all values of Z, and the value $Z = 6$ has therefore been chosen to fit the main part of the curve.

It is evident that either equation represents the main features of the curve extremely well, and confirms the essential correctness of the method of calculation. Since no specific assumptions have been made regarding the chemical nature of either the solvent or the polymer, the same entropy of dilution should be found for any other solvent–polymer system, provided only that the polymer molecule is sufficiently flexible to justify the assumption of very small segments. Experimental data by which this might be checked are lacking, and the best we can do is to compare values of $-\Delta G_0/T$ obtained from vapour-pressure data,* with the theoretical curve for ΔS_0. Three such comparisons are included in Fig. 3 and conform very closely to the expected behaviour. If $\Delta H_0 > 0$, we have $-\Delta G_0/T < \Delta S_0$, and this is seen to be the case for toluene and acetone. The toluene curve is almost identical with the corresponding curve for benzene, and the larger displacement of the acetone curve agrees with the much greater heat of dilution to be anticipated. It is noteworthy that the chloroform curve lies above the theoretical entropy curve: this is to be expected, since Hock and Schmidt[35] have shown that $\Delta H_0 < 0$.

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[34] *Kolloid-Z.*, 1929, **47**, 294.

[35] L. Hock and H. Schmidt, *Rubber Chem. and Techn.*, 1934, **7**, 462; S. Boström, *Kolloid-Beih.*, 1928, **26**, 439.

[36] G. Gee, *Trans. Faraday Soc.*, 1942, **38**, 418.

* ΔG_0 is the Gibbs free energy of dilution, equal to $\Delta H_0 - T\Delta S_0$.

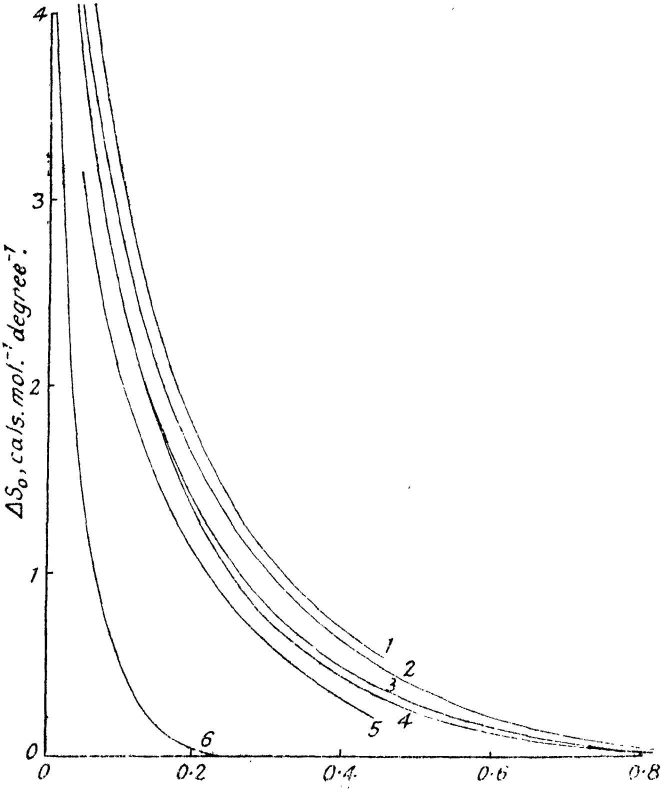

FIG. 3.

Entropy of Dilution of Rubber Solutions.

Curve.	Source.	Ref.
1	$-\Delta G_0/T$ for $CHCl_3$	37
2	Theoretical (Flory)	22
3	Theoretical (Miller)	26
4	Experimental: benzene	19
5	$-\Delta G_0/T$ for toluene	32
6	$-\Delta G_0/T$ for acetone	37

On the assumption of an entropy of dilution given by one of the theoretical equations, it is possible to make considerable progress in understanding other properties of rubber solutions and gels. Before this work can be described, it is necessary to consider another method of investigating the size and shape of rubber molecules, *viz.*, the measurement of solution viscosities.

[37] J. Lens, *Rec. Trav. chim.*, 1932, **51**, 971.

The Viscosity of Rubber Solutions.

It is not proposed to discuss at length the general problem of the viscosities of high-polymer solutions, since a number of recent articles have been devoted to this topic.[38] We shall be concerned with the problem only in so far as it bears on the determination of the size and shape of rubber molecules.

Two general methods have been adopted in discussing the viscosity of polymer solutions. The first treats the suspended particle (molecule) as a rigid ellipsoid, whose axial ratio is calculated from the experimental data.[38a] This model is so far removed from our concept of the rubber molecule in solution that it does not seem profitable to discuss it further in this Report. The other method attempts to relate the viscosity of a dilute solution with the molecular weight of the solute. The possibility of doing so depends on the assumption of Staudinger's law, or some modification of it. As originally proposed,[39] it took the form

$$\eta_{\mathrm{sp.}} = k_m c M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where $\eta_{\mathrm{sp.}}$ is the specific viscosity of a solution of concentration c, and k_m is a constant. Since it is found that $\eta_{\mathrm{sp.}}/c$ is always dependent on c, it is customary to employ the value extrapolated to infinite dilution. This quantity was termed by W. D. Lansing and E. D. Kraemer[40] the "intrinsic viscosity" $[\eta]$, and by H. Staudinger, H. Berger, and K. Fischer,[41] the "viscosity number" Z_η. It has also been clearly recognised that $(1/c) \ln \eta_r$ is much less dependent on c than is $\eta_{\mathrm{sp.}}/c$,[42] so the most convenient form of equation is

$$M = K \lim_{c \to 0} \left(\frac{1}{c} \ln \eta_r\right) = K[\eta] \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where $\eta_r = 1 + \eta_{\mathrm{sp.}}$ is the relative viscosity of the solution. Equation (21) might be justifiable in one of two ways: (*a*) by an acceptable theoretical derivation, or (*b*) by comparing intrinsic viscosities with molecular weights measured in other ways.

A very clear discussion of the factors involved in the shear of a liquid containing non-spherical particles is given by Lawrence.[38b] Rigid elongated particles increase the viscosity of a solution when the two ends of a particle are situated in layers of the liquid which, as a result of sheer, are moving at different rates. There is a tendency to stretch the particle and to rotate it into the streamlines. Orientation is, however, upset by Brownian motion, and a certain mean orientation results from the interplay of these two forces. At high rates of shear, orientation becomes increasingly perfect, whereas a rise of temperature favours disorientation. Furthermore, it is evident that maximum disturbance of flow will occur when the particle lies directly across the streamlines, flow being quite undisturbed by thin particles if perfectly oriented. These considerations provide a ready explanation of J. R. Robinson's observations[43] on the viscosity of solutions of tobacco mosaic virus. The viscosity falls rapidly as the rate of shear is increased, and in a typical capillary viscometer of the Ostwald type it is much smaller than in a Couette viscometer, in which the rate of shear can be made very small.

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[38] (*a*) J. M. Burgers, " Second Report on Viscosity and Plasticity " (Amsterdam, 1938); (*b*) A. S. C. Lawrence, *Ann. Reports*, 1940, **37**, 99; (*c*) F. Eirich, *Reports Progr. Physics*, 1940, **7**, 329.

[39] Staudinger, *op cit.*

[40] *J. Amer. Chem. Soc.*, 1935, **57**, 1369.

[41] *J. pr. Chem.*, 1942, **160**, 95.

[42] A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, 1941, **33**, 1263.

The application of these ideas to rubber solutions requires us to know the form of the rubber molecule in solution. Tobacco mosaic virus is known to consist of rigid rods, but Staudinger's original suggestion[39] that all polymer molecules were similarly rigid has long been rejected. The chemical nature of rubber leads inevitably to the conclusion that the molecule must possess a high degree of freedom of rotation about the single bonds in its structure. As a result of this freedom, a fully extended configuration is extremely improbable, and *in the absence of any restraining force* the molecule will assume a series of constantly changing, randomly kinked forms, in which the average distance between its ends is far less than the maximum possible. A statistical analysis of the most probable molecular configuration has been attempted by a number of workers[44] and an account of their work is given in a recent report.[45] It will suffice here to point out that all treatments, in addition to other approximations, involve the assumption that all configurations formed by rotations about a single bond are of equal energy.

M. L. Huggins[46] has attempted to calculate the viscosity of a solution of long-chain molecules along the following lines. The molecule is treated as a chain of "submolecules," whose distribution is given by equations analogous to those of Kuhn.[44] Each submolecule is, in general, moving with a velocity different from that of the layer of liquid with which it is in contact. This relative velocity is calculated, and the work done on the liquid by the submolecule estimated by means of Stokes's law. A summation over all the submolecules gives the total work done, and hence the contribution of the molecule to the viscosity of the solution.

The result of this calculation is to give a relationship between viscosity and molecular weight which, for long molecules, reduces to the form of equation (21), a definite value being given to the constant K in terms of atomic parameters. This theoretical treatment is undoubtedly a great advance on any other attempt to solve the problem, and goes far to suggest that Staudinger's law should be approximately valid for rubber solutions. An evident source of error is the assumption that the molecular shape distribution will be unaffected by suspending the molecule in a liquid undergoing shear. Huggins has suggested that the correction is likely to be small, but a fuller analysis is desirable. Experimentally the problem could be largely solved by studying the viscosity of rubber solutions over a wide range of rates of shear. A more serious objection to this treatment is inherent in Kuhn's distribution function. Since the molecule is idealised to a series of points, the effect of molecular size is neglected, and the calculated distribution must be much more compact than the real one. It follows that Huggins's calculated viscosity must be too small, but *provided* that only the value of the constant K be thereby affected, the main conclusion of Huggins's analysis will still be valid.

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[43] *Proc. Roy. Soc.*, 1939, *A*, **170**, 519.

[44] R. Kuhn, *Kolloid-Z.*, 1934, **68**, 2; E. Guth and H. Mark, *Monatsh.*, 1934, **65**, 93.

[45] L. R. G. Treloar, *Reports Progr. Physics*, 1942, **9** (in press).

[46] *J. Physical Chem.*, 1938, **42**, 911; 1939, **43**, 439; *J. Appl. Physics*, 1939, **10**, 700.

Theory thus gives us reason to think that equation (21) should be *approximately* valid, and most workers would agree that the experimental evidence leads to the same conclusion. The use of viscosities for molecular-weight determination is, however, only possible if equation (21)—or some other—holds *accurately*. This can at present only be tested experimentally, and as we shall see, there is no consensus of opinion about the results. Before giving the experimental results, a number of other theoretical points must be mentioned.

In a rubber solution there exist molecules covering a range of molecular lengths, and the "molecular weight" of the rubber is therefore to be interpreted as a mean value. If we have n_i molecules of molecular weight M_i, the mean molecular weight $M_{\mathrm{osm.}}$, as ordinarily understood, is given by

$$M_{\mathrm{osm}} = \sum_i n_i M_i / \sum_i n_i$$

This equation is valid for molecular weights determined by the osmotic method, but it can be readily shown [47] that, if Staudinger's law holds for each component of a mixture, the mean viscosity molecular weight M_v of the mixture is given by

$$M_v = \sum_i n_i M_i^2 / \sum n_i M_i$$

It will be evident that $M_v > M_{\mathrm{osm.}}$ and that the ratio $M_v/M_{\mathrm{osm.}}$ is a measure of the degree of homogeneity of the rubber. There are two ways of avoiding this difficulty in order to test equation (21). One is to compare viscosities with ultracentrifuge data, which can be employed to calculate M_i;[40] the other is to fractionate rubber so as to obtain materials as homogeneous as possible, and then to compare the viscosity with the osmotic molecular weight.

A second difficulty arises from the possible existence of branches in the molecular chain of rubber. Although there is no evidence of this from other sources, it is difficult to point to any fact which conclusively disproves the possibility. Now, it is clear that in general a molecule possessing a branched structure will take up a more compact form than a truly linear molecule, and will therefore contribute less to the viscosity. It has therefore been suggested (see below) that viscosity measures the length of the main chain, and will only be comparable with the other molecular-weight methods in the case of linear molecules. This argument is not very convincing, for although it may be true that a short side chain contributes little to the intrinsic viscosity, yet the effect of the long side chains, implied by the concept of branching, cannot be negligible. Qualitatively, however, it is clear that branching should reduce [η], and therefore invalidate the method.

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[47] Lansing and Kraemer, ref. (40).

The last difficulty we shall discuss is that of the effect of solvent. The theory as formulated predicts that $[\eta]$ should be the same in all solvents, which is well known to be untrue. A satisfactory theory must give some explanation of this anomaly, and also suggest the best solvent for viscosity measurements. It seems probable that the different values of $[\eta]$ found in various solvents are to be associated with different forms taken up by the molecule in solution.[48] This would not be difficult to understand, for it is only in a solvent in which rubber forms ideal solutions ($\Delta H_0 = 0$) that the various possible configurations of the molecule can have equal energy. Now this is a primary assumption in calculating the entropy of solution as described earlier. If $\Delta H_0 > 0$, the total energy of the system (rubber and liquid) will be reduced by the molecules taking up more compact configurations, so as to reduce the interface rubber/liquid. Despite the lower entropy of such a state, the net effect will be a reduction of free energy. It is clear, therefore, that the larger ΔH_0 becomes, the more compact will be the mean molecular configuration, and the lower the solution viscosity. If, on the other hand, $\Delta H_0 < 0$, extended configurations become favoured, and solutions of high viscosity are to be expected. Although, as already noted, few values of ΔH_0 are available, we shall see later how they may be estimated, and the data are in general agreement with the prediction that $[\eta]$ should fall with ΔH_0. Since the theory is worked out for $\Delta H_0 = 0$, we have also a criterion for selecting the best solvent, though in a later section it will be shown that other conditions may in practice need to be considered.

The first experimental data to be considered are those in which intrinsic viscosity has been compared with osmotic molecular weight. The evaluation of this evidence depends to a considerable extent on the method employed in extrapolating the osmotic data, and it is clear that the same method must be applied to all the data. The figures given in Table II are based on the method described above, the actual extrapolations for toluene being shown in Fig. 2. Values in parentheses are those given by the original authors, and the effect of different methods of extrapolation is only too evident.

TABLE II.

Comparison of Intrinsic Viscosity with Osmotic Molecular Weight.

Material.	Viscosity solvent.	Ref.	$10^{-5}M_{\text{osm.}}$	$[\eta]$.	$10^{-4}M/[\eta]$.
(1) *Fractionated rubbers :*					
Intermediate latex fraction	Benzene	29	3·5	5·8	6·0
Low latex fraction	,,	29	2·1	4·0	5·3
Hydrocarbon from oxide fraction	,,	29	0·66	1·02	6·5
(2) *Unfractionated rubbers :*					
Crepe (acetone extracted)	Benzene	29	2·6	$5{\cdot}7_5$	4·5
" Sol " rubber	,,	29	3·0	$5{\cdot}7_5$	5·2
,, ,, ...	Toluene	5	$1{\cdot}8_5$ $(2{\cdot}4_5)$	3·8	4·9 (6·4)
Purified with Al_2O_3	,,	5	3·6 (3·5)	8·4	4·3 (4·2)
Lightly milled crepe	,,	49	1·6 (2·7)	3·7	4·3 (7·3)

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[48] T. Alfrey, A. Bartovics, and H. Mark, *J. Amer. Chem. Soc.*, 1942, **64**, 1557; cf. ref. (22).

[49] K. H. Meyer, *Helv. Chim. Acta*, 1941, **24**, 217.

On the basis of the data for the fractions, Gee [29] suggested that Staudinger's law holds for rubber within the accuracy (*ca.* 10%) with which it can at present be tested, at any rate over the molecular weight range 60,000—350,000. Subsequent work (see below) has led to the conclusion that these fractions were much less homogeneous than was thought at the time, so that one might expect the ratio $M/[\eta] = 6{\cdot}_0 \times 10^4$ to be somewhat too low. On the other hand, the data available have now been considerably extended, and confirm the original conclusion that, for rubbers of high molecular weight, $[\eta] \propto M$, with a constant of proportionality close to that previously found. The ratio $M/[\eta]$ for unfractionated rubbers is seen from Table II to be somewhat lower than for the fractions, in agreement with their wider range of molecular weights. (It will be noted that if the published osmotic molecular weights are employed this last statement is untrue.)

The other possible way of testing the Staudinger law in the high-molecular region is by comparison of intrinsic viscosity with ultracentrifuge molecular weights, which may be done for any rubber, whether homogeneous or not. No systematic work has been done on these lines, but Kraemer [50] has reported the results given in Table III.

TABLE III.

Comparison of Intrinsic Viscosity with Ultracentrifuge Molecular Weight.

Material.	Viscosity solvent.	$10^{-5}M$ (in ether).	$[\eta]$.	$10^{-4}M/[\eta]$.
Sol A	Ether	4·00	1·85	21·5
	Benzene	—	2·60	15·5
Sol B	Ether	4·35	2·05	21
	Benzene	—	3·74	11·5
Low viscosity rubbers	Ether	0·69	$0{\cdot}34_2$	20
	$CHCl_3$	0·635	$0{\cdot}50_7$	12·5

It is difficult to discuss these figures, since they were presented without experimental details beyond a statement that the sedimentation equilibrium method was employed. Considering the viscosity in ether, we find support for the Staudinger equation. The intrinsic viscosities measured in benzene are not accurately proportional to M, and the ratios of $M/[\eta]$ are approximately twice as high as those found from osmotic data. This discrepancy requires further investigation, but it is relevant to point out that the difficulty of reconciling osmotic and ultracentrifuge data is not confined to rubber. R. Signer and H. Gross [51] have used the sedimentation equilibrium method to estimate the molecular weights of some polystyrene fractions in chloroform, obtaining values which are proportional to $[\eta]$. They point out that the calculation requires the assumption of van't Hoff's law, and give the apparent molecular weight of one fraction ($M = 3 \times 10^5$) as a function of concentration. The deviation from van't Hoff's law revealed by these figures may be expressed in terms of the calculated osmotic pressures.

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[50] " The Ultracentrifuge " (Oxford, 1940), p. 423.

[51] *Helv. Chim. Acta*, 1934, **17**, 335.

$10^4\Pi/c$ is found to rise from 0·73 at infinite dilution to 2·9 at a concentration of 2·5 g./l. Schulz [12] gives osmotic data for a polystyrene fraction in toluene, which show $10^4\Pi/c$ increasing, over the same concentration range, from 0·73 to 0·87. Although it is true that the slope of the Π/c–c curve is probably higher for chloroform than for toluene (ΔH_0 is probably negative for chloroform), yet there seems a definite discrepancy here. Almost the whole of the work on the ultracentrifuge has been carried out with aqueous solutions, and it is perhaps better to suspend judgment on the above results until more extensive experience has been gained of the technical difficulties encountered with non-aqueous solutions.

No other method is available for testing the applicability of Staudinger's equation to high-molecular rubbers, but if we *assume* its validity, the constant may be determined by reference to lower members of the series. By comparing intrinsic viscosities with molecular weights determined cryoscopically, we can test the equation for low-molecular rubbers and, if it proves valid in this region, employ the constant thus obtained for rubbers of much higher molecular weight, *assuming* the possibility of the enormous extrapolation involved. This is the method first employed by H. Staudinger and H. F. Bondy,[52] and subsequently adopted and refined by A. R. Kemp and H. Peters.[53] The former workers used crude degradation products obtained by heating tetralin or xylene solutions of rubber in air; the latter started from similar materials, but subsequently fractionated them, obtaining in this way a range of products of low molecular weights, but containing various amounts of oxygen (up to nearly 6%) and with rather low iodine values. Some of these materials became insoluble on heating in a vacuum to 100°, probably owing to a form of cross linking or oxygen vulcanisation. Since all their products were treated in the same way, there is a considerable assumption involved in regarding them simply as low-molecular homologues of rubber. Intrinsic viscosities in benzene were compared with cryoscopic molecular weights determined in benzene or *cyclo*hexane. The calculated molecular weight was substantially independent of concentration for $M < 2000$, but for the higher fractions deviations occurred which are, of course, parallel to those found in the osmotic data. The authors reject all such results as " unreliable," but in view of our conclusion that extrapolation to infinite dilution leads to the correct molecular weight, there is evidently no basis for this selection. Table IV summarises their results, molecular weights marked * having been obtained by extrapolation. Data are included for squalene, a hexamer of isoprene, of known constitution.

Considering only the lower fractions to be reliable, Kemp and Peters take $M/[\eta] = 2{\cdot}2 \times 10^4$, which they then use in equation (21) to calculate much higher molecular weights. The disagreement of the results with the osmotic data is ascribed to the errors in the latter. From the point of view set out in this Report, all the figures of Table IV are equally trustworthy. Since they reveal an obvious trend of $M/[\eta]$ with M, they must, in the Reporter's opinion, lead to the conclusion that Staudinger's law does not hold accurately

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[52] *Ber.*, 1930, **63**, 734.

[53] *Ind. Eng. Chem.*, 1941, **33**, 1263, 1391.

TABLE IV.

Comparison of Intrinsic Viscosity in Benzene with Cryoscopic Molecular Weight.

Material.	$10^{-5}M$.	$[\eta]$.	$10^{-4}M/[\eta]$.
Squalene [54]	0·00410	0·023$_0$	1·8
Fraction 3	0·012	0·058	2·1
Acetone-soluble, washed with alcohol	0·014$_2$	0·065	2·2
Fraction 4	0·064 *	0·198	3·2
Fraction 5	0·090 *	0·262	3·4$_5$

for low-molecular materials. This behaviour is not confined to rubber, but has been found in all series of materials whose viscosities have been studied down to the low-molecular-weight region.[55] Several types of explanation have been proposed :

(*a*) Kemp and Peters reject cryoscopic and osmotic data for solutions which do not obey van't Hoff's law, and *assume* Staudinger's law to hold.

(*b*) Staudinger and Fischer [5] accept the osmotic data as correct, but also assume the validity of the viscosity law and derive a constant in the same way as Kemp and Peters. Where the latter leads to molecular weights lower than those measured osmotically, the material is assumed to be branched. Arguing that viscosity is a measure of molecular length, these authors define the degree of branching as $M_{\text{osm.}}/M_v$. Unless evidence of branching is forthcoming from other sources, it seems preferable to seek another explanation of the data.

(*c*) Most workers now accept the evidence at its face value, and thus conclude that Staudinger's law is *not* accurately obeyed, even by homogeneous, linear polymers. Two modifications of the equation have been suggested. Except for very low M, the data for the polyesters [55] obey an equation of the form :

$$M = K[\eta] + K' \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

A more radical modification has recently been proposed by R. Houwink : [56]

$$M = K[\eta]^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

P. J. Flory [57] has reported that this equation holds for polybutenes between $M = 5 \times 10^3$ and 5×10^5, giving $n = 1{\cdot}65$. We may seek to apply these equations to rubber by combining the data of Tables II and IV. A fairly good fit is given by equation (23) if we take $K = 4{\cdot}2 \times 10^4$, $n = 1{\cdot}23$, but the lowest of the osmotic points is badly out. Equation (22) is very little better than (21).

Summarising, it is evident that the precise relationship between molecular weight and the intrinsic viscosity of rubber solutions over a wide range of M remains to be determined. The principal experimental difficulty to be overcome is that of obtaining rubbers of medium and low molecular weight which we can confidently assume to be linear and reasonably homogeneous. Until this can be done, the extension of the Staudinger equation beyond the molecular weight range 60,000—350,000 is dangerous. Within that range, the Reporter's opinion is that equation (21) may be applied to intrinsic viscosities measured in benzene solution, using $K = 6{\cdot}0 \times 10^4$, and that the molecular weights thus obtained are probably accurate to within 10 or 20%.

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[54] Staudinger and H. P. Mojen, *Kautschuk*, 1936, **12**, 121.

[55] *Polyesters :* P. J. Flory and P. B. Stickney, *J. Amer. Chem. Soc.*, 1940, **62**, 3032; W. O. Baker, C. S. Fuller, and J. H. Heiss, *ibid.*, 1941, **63**, 2142. *Polyoxyethylene glycols :* R. Fordyce and H. Hibbert, *ibid.*, 1939, **61**, 1912.

[56] *J. pr. Chem.*, 1940, **157**, 15.

[57] *Indiarubber World*, 1942, **106**, 584.

We now discuss the use of solvents other than benzene for the measurement of intrinsic viscosities. Gee [49] has presented data which show that, within the molecular weight range 60,000—350,000, the intrinsic viscosities in a number of solvents are accurately proportional; *i.e.*, if the Staudinger law is valid for benzene, it is also valid for any of the other solvents examined, provided that the appropriate constant be used for each. A. R. Kemp and H. Peters [58] have recently shown that this is by no means true over a wide range of molecular weights, in the case of poly*iso*butylene. For instance, with $M = 1000$, the intrinsic viscosities in *cyclo*hexane, carbon tetrachloride, hexane, chloroform, and benzene are in the ratios 127, 118, 100, 100, 85. With $M = 10^5$ these values become 140, 120, 100, 100, 38, the intermediate variation being nearly linear with log M. With $M < 1000$ very large changes occur in the ratios, and it is evident that if Staudinger's law holds in this region for hexane solutions (taken as standard by Kemp and Peters) it cannot also hold for the other solvents.

No explanation has been offered of the curious behaviour of low-molecular rubbers in different solvents, though Burgers [38] has pointed out that the viscosities of solutions of some of the paraffins studied by K. H. Meyer and A. J. A. van der Wyk [59] are *lower* than those given by A. Einstein's equation for *spherical* molecules. The intrinsic viscosities of high-molecular rubbers are readily interpreted on the basis of the theory already discussed. Although the heats of mixing of rubber with various solvents are unknown, yet there is reason to believe (see below) that the degrees of swelling, Q, of a vulcanised rubber in a series of solvents run closely parallel with their heats of dilution. We should therefore expect the intrinsic viscosities of a sample of rubber to be a simple function of the degrees of swelling. In Table V some swelling data given by G. S. Whitby, A. B. A. Evans, and D. S. Pasternach [60] are compared with intrinsic viscosities found by Kemp and Peters [53] and Gee.[29]

The parallelism is evidently not exact, particularly in the case of the more polar liquids, but is sufficiently good to lend general support to the theory.

It was suggested earlier that the ideal viscosity solvent would be one for which $\Delta H_0 = 0$. Probably *cyclo*hexane falls nearest to this condition, but is well known to disperse rubber with some difficulty (see below). Being a somewhat viscous liquid, it also leads to highly viscous solutions, which are evidently undesirable. Benzene lies next to *cyclo*hexane in the table, and is a very satisfactory rubber solvent. It is therefore the Reporter's first choice as the standard liquid for the determination of intrinsic viscosities of rubber solutions.

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[58] *Ind. Eng. Chem.*, 1942, **34**, 1192. [59] *Helv. Chim. Acta*, 1935, **18**, 1067.

[60] *Trans. Faraday Soc.*, 1942, **38**, 269.

TABLE V.

Intrinsic Viscosites and Swelling Power.

Liquid.	Q (c.c. liquid per c.c. rubber).	Relative intrinsic viscosities.	
		Kemp and Peters.	**Gee.**
Carbon tetrachlorde	5·0 *	112	—
Chloroform	4·2 *	107	—
Toluene	4·2	103	—
Benzene	3·9	(100)	(100)
*cyclo*Hexane †	—	98	104
Amyl acetate	1·8	—	58
Ethyl ether	1·6	—	64
Hexane	1·2	88	—

* Unpublished data, quoted by kind permission of Prof. Whitby.

† Q not measured, but almost certainly occupying this position in the table (by comparison with swelling in other liquids).

Solubility and Fractionation.

Two main lines of attack on this problem may be distinguished : (*a*) an experimental study of the behaviour of rubber towards various solvents, and (*b*) recent attempts to explain the main features of these results by a theoretical approach. It will be convenient in this Report to reverse the historical order, so as to be able to use the results of the calculations in discussing the significance of the experimental work.

J. N. Brønsted [61] was one of the first to suggest a plausible explanation of the unusual solubility relationships of high polymers. He argued that the distribution of *large* polymers between two phases would be determined almost entirely by the difference of potential energy between them. Assuming this to be proportional to the molecular weight of the polymer, he obtained for the relative concentrations c' and c'' of polymer in two phases in equilibrium

$$\ln c'/c'' = \lambda M/RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where λ is a constant, characteristic of the solvent and the series of polymers considered. If M is large it is readily seen that the ratio c'/c'' may assume extreme values. Considering λ as continuously variable along a series of liquids, it is clear that, as λ decreases through zero and becomes negative, the distribution undergoes a sudden change of character. With $\lambda > 0$, $c'/c'' \longrightarrow 0$, and the liquid is practically a non-solvent; with $\lambda < 0, c'/c'' \longrightarrow \infty$, and the liquid is a perfect solvent. This prediction accords with Brønsted and Volquartz's work on the solubility of high-molecular polystyrenes [62] which shows a very sharp separation of liquids into non-solvents and perfect solvents. Schulz [63] extended this concept to mixed liquids, by assuming in this case that λ is a linear function of the liquid composition.

By considering a mixture of solvent and non-solvent, the proportion γ

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[61] *Z. physikal. Chem.*, 1931, Bodenstein Festband, p. 257; *Compt. rend. Lab. Carlsberg*, Sér. chim., 1938, **22**, 99.

[62] Brønsted and K. Volquartz, *Trans. Faraday Soc.*, 1940, **36**, 619.

[63] *Z. physikal. Chem.*, 1937, *A*, **179**, 321.

of the latter in the critical mixture which is *just* a solvent was shown to be given by an equation of the form

$$\gamma = A + B/M \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where A and B are constants. This equation has been shown to represent satisfactorily the data for a number of synthetic polymers.[64]

Notwithstanding the apparent success of these theories, it has been pointed out by Gee and Treloar [19] that their fundamental assumption is unsound. These authors showed experimentally that the molar entropy of solution of rubber in benzene is large compared with the heat of solution, and that it is proportional to the molecular weight of the rubber. Equations (24) and (25) therefore require another explanation; a possible one is suggested below.

The equilibrium distribution of rubber between two phases has also been examined by Flory,[22] Huggins,[23] and Gee.[65] The conditions for equilibrium between two phases $'$ and $''$ may be put in the form

$$\left.\begin{aligned} \Delta G_0' &= \Delta G_0'' \\ \Delta G_r' &= \Delta G_r'' \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

where the subscripts $_0$ and $_r$ refer respectively to liquid and to rubber.* The free energies are then expressed in terms of the heats and entropies of mixing. The latter is taken to be that given by the calculations described in the first section of this report, but a simple-power law is usually assumed for the heat. Thus, Flory writes, for each phase :

$$\begin{aligned} \Delta G_0 &= \Delta H_0 - T\Delta S_0 \\ &= kv_r^2 + RT\{\ln v_0 + v_r\,(1 - M_0/M)\} \\ \Delta G_r &= kMv_0^2/M_0 + RT\{\ln v_r - v_0\,(M/M_0 - 1)\} \quad . \quad . \quad (27) \end{aligned}$$

The assumption involved in writing down these equations is that the rubber may be treated simply as a liquid, a point of view which finds justification both in its mechanical properties (which demonstrate the great freedom of the molecules to move relative to one another) and in the agreement with this theory found experimentally by Gee and Treloar. If equation (27) is used to give the free energies in terms of composition, equations (26) give two simultaneous equations from which v_r' and v_r'', the concentrations of rubber in the two phases, may be calculated. No simple algebraic solution is possible, but Flory has given a graphical solution for several values of k. His conclusion is that, for any value of k, there exists a critical temperature above which rubber is miscible with the liquid in all proportions. The composition of the critical mixture is given by

$$(v_r)_{\text{crit.}} = 1/(\sqrt{M/M_0} + 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

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[64] R. A. Blease and R. F. Tuckett, *Trans. Faraday Soc.*, 1941, **37**, 571; cf. also refs. (55), (63).

[65] *Ibid.*, 1942, **38**, 276.

* $\Delta G_r'$ is the increase of Gibbs's free energy when 1 mole of rubber is added to a large bulk of phase $'$.

Since, for rubber, $M/M_0 \simeq 4 \times 10^4$, $(v_r)_{\text{crit.}} \simeq 0{\cdot}015$. At a lower temperature, a two-phase system results, in which the dilute phase has a concentration $< (v_r)_{\text{crit.}}$. Indeed, except within a few degrees of the critical temperature, the dilute phase would be indistinguishable experimentally from pure solvent. The concentrated phase consists of a highly swollen gel, in which the calculated rubber content at a temperature 10° below the critical is only 10%.

A similar analysis was carried through by Gee,[65] using a more complex expression for the heat of mixing, *viz.*,

$$\Delta H_0 = \alpha(1 + \beta) M_0[v_r/(1 + \beta v_0)]^2 \quad . \quad . \quad . \quad . \quad (29)$$

The essential features of the solution are the same as in that of Flory, but it is possible to have a two-phase system in which the two phases are considerably more concentrated than is permitted by Flory's analysis.

It is of interest to try to find the relationship between this method of analysis and Brønsted's equation (24), since the latter has in practice proved so useful. If this equation were strictly true, it should be derivable from the solution of equations (26) and (27). Although this cannot be done rigorously, a similar equation may be derived by the following approximate method.

Combining the second equilibrium condition of equation (26) with (27) we obtain

$$\ln \frac{v_r'}{v_r''} = -\frac{kM}{M_0\boldsymbol{RT}}\{(v_0')^2 - (v_0'')^2\} + (v_0' - v_0'')\left(\frac{M}{M_0} - 1\right) \quad . \quad (30)$$

The phase $'$ represents a dilute solution, for which we may write $v_0' \simeq 1$. The results of the complete analysis described above show that the composition of the second phase is almost independent of M. This is confirmed by experiment,[63] so that v_0'' may be treated as a constant. Equation (30) thus takes the form

$$\ln v_r'/v_r'' = M(a - b/\boldsymbol{RT}) \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where $a = (1 - v_0'')/M_0$; $b = k\{1 - (v_0'')^2\}/M_0$. The functions a and b will not be strictly independent of T, and it is evident that equation (31) differs formally from (24) only in predicting a more complex dependence on temperature. In fact, it is precisely in regard to temperature variation that Schulz's equation fails.[63] This analysis thus provides a reason for the formal success of the Brønsted–Schulz equations, while at the same time giving a different, and more satisfactory, interpretation of the constants.

The analysis described so far has considered the rubber as homogeneous, and we have now to enquire what modifications result when a mixture of rubbers of different molecular weights is present. In the course of a fractionation by any equilibrium method (see below) we obtain two phases, each containing a portion of the rubber. The problem is to calculate the molecular-weight distribution in the two fractions, given that of the total rubber. Schulz examined this problem by assuming that the distribution of each molecular species $_i$ between the two phases was given by a modification of equation (24), which may be written :

$$\ln c_i'/\alpha c_i'' = -\lambda M_i/\boldsymbol{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

α was treated as an empirical constant, characteristic of the solvent and polymer and independent of M_i. By applying this equation to a range of M_i values, Schulz obtained graphically distribution curves for the fractions resulting from separating a rubber of given molecular distribution under various conditions. An important practical conclusion was that the efficiency of separation should be improved by keeping the concentration of the dilute phase as low as possible. There is no obvious justification for the arbitrary introduction of the constant α, and it should be further pointed out that this theory makes no attempt to examine the mutual effect of the different rubbers on their several solubilities. In order to solve the problem completely, we require to know the entropy of mixing ΔS^m of n_0 solvent molecules with n_i rubber molecules of molecular weight M_i, where $_i$ is to be given all values. Gee [65] suggested for this purpose an empirical extension of Flory's equation [22] to give the form :

$$\Delta S^m = -k\{n_0 \ln v_0 + \Sigma n_i \ln v_i\} \quad . \quad . \quad . \quad . \quad (33)$$

On this basis, it was shown that the distributions of two molecular species $_i$ and $_j$ between the two phases were related by the equation

$$\frac{1}{M_i}\ln\frac{v_i'}{v_i''} = \frac{1}{M_j}\ln\frac{v_j'}{v_j''} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Extended to a wide distribution of rubbers, this analysis [67] confirms Schulz's findings [66] regarding the effect of concentration on the efficiency of fractionation, and indeed leads to the conclusion that a " fractionation " in which the concentration of the dilute phases exceeded 1% would effect scarcely any separation at all, even of a complex mixture. The practical importance of such a conclusion requires no emphasis.

Before describing the experimental data, we may enquire how far the analysis would be expected to apply to rubber. The first criticism to be made is a general one. We have found, in the viscous behaviour of rubber solutions, evidence that the entropy of solution is less in a bad solvent (ΔH_0 large) than in a good one. It is clear, therefore, that an approximation is involved in assuming the entropy of mixing, which is calculated for an ideal solvent, to apply to a liquid on the borderline between solvent and non-solvent. Again, much of the work on solubility has been carried out with mixtures of solvent and non-solvent. Hitherto, such a mixture has been treated simply as a single liquid, whose properties are intermediate between those of its constituents. Actually, this is only valid to a first approximation, since in general the two liquids are differently distributed between two phases in equilibrium.[62] No systematic study of such a system has yet been published. A final point is that, throughout the analysis, we are concerned either with a homogeneous material or with a homologous series of similar polymers. This is doubtless a very good approximation in the case of many synthetic polymers, but rubber, as normally handled, is far from being adequately described in this way. The protein present in latex is most tenaciously retained by the solid rubber, and may profoundly modify its solubility behaviour. In many cases, as we shall see, its effect may well be so large as to mask entirely the effect of molecular weight differences.

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[66] G. V. Schulz, *Z. physikal. Chem.*, 1940, *B*, **46**, 105, 137; **47**, 155.

[67] G. Gee, unpublished calculations.

Rubber has long been known to be capable of separation, by treatment with solvent, into portions of very different solubility. It was formerly considered[68] that two sharply defined portions termed " sol " and " gel " were present, of which only the former was soluble. The usual method of separating these consists in extraction with light petroleum, or ethyl ether, but a careful study of the process[69] revealed that the boundary was ill defined, and that the sol portion was greatly diminished if care was taken to exclude oxygen. Kemp and Peters found that only 4—10% of some of the rubber samples they examined was extracted by hexane after 3 days. Using other extractants,[70] they obtained much larger amounts of " sol," but even chloroform (the best liquid tried) extracted only 62% of latex film after 3 days at 25°, without shaking. Actually, all samples of raw rubber examined by the Reporter could be completely dispersed in solvent if sufficient time was allowed, and agitation employed, although oxygen was rigorously excluded.

The failure of rubber to disperse easily and completely in hydrocarbon solvents is very surprising, and quite inexplicable if we regard rubber merely as a mixture of long straight-chain hydrocarbons. As we have noted above, *cyclo*hexane should be a perfect solvent for rubber, but in fact even a purified rubber hydrocarbon disperses with some difficulty, giving " ropy " solutions at relatively low concentractions. Benzene is considerably superior in this respect, although the rubber is more easily precipitated from it by alcohol than from *cyclo*hexane.[71] A still better solvent, from the point of view of obtaining clear mobile solutions, is a mixture of benzene with several per cent. of an alcohol. Such a mixture disperses " gel " rubbers which are insoluble in benzene alone, while small additions of alcohol greatly increase the solvent power of hexane.[70] It appears probable that we are dealing here with two distinct factors. The lack of fluidity in the solvent which is best thermodynamically (*i.e.*, for which $\Delta H_0 = 0$) arises from the greater space occupied by the average molecule in such a solvent (cf. discussion on viscosity, above), which leads to structural viscosity. Addition of alcohol reduces this effect, and at the same time assists in separating the chains where they are held by the polar interactions between protein molecules.

It is quite unnecessary to assume, with Kemp and Peters, that sol rubber is necessarily an oxidation product of gel rubber. It is well known that oxidation promotes degradation of the rubber chains to more soluble products, but there is every reason to believe—from the thermodynamic study of Gee and Treloar[19]—that a linear, unoxidised rubber of *any* molecular weight would be completely soluble in benzene. The fact that complete solution of rubber can be achieved experimentally also rules out the possibility of insolubility arising from chemical cross links between the molecules. The final suggestion is that the protein remaining in association with the rubber is connected with the difficulty of dispersing it. Direct evidence that this is the true explanation is provided by the well-known fact [69] that the gel rubber contains practically the whole of the nitrogen. The nature of the association between rubber and protein is unknown, but its profound effect on the solubility of rubber is evident when we examine the various attempts which have been made to fractionate rubber.

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[68] For a review, see G. S. Whitby, *Trans. Inst. Rubber Ind.*, 1929, **5**, 184.

[69] W. H. Smith and C. P. Saytor, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 453; A. R. Kemp and H. Peters, *J. Physical Chem.*, 1939, **43**, 923, 1063.

[70] *Idem, Ind. Eng. Chem.*, 1941, **33**, 1391.

[71] H. Staudinger and H. P. Mojen, *Kautschuk*, 1936, **12**, 121.

Two general methods of fractionation have been adopted, based severally on the greater speed of solution of the shorter molecules, and on their greater solubility in critical mixtures of solvent and non-solvent. In almost all cases the initial material used contained appreciable percentages of nitrogen, and there is abundant evidence that this is a complicating, if not actually the controlling factor. This is shown very clearly in the early work of T. Midgley, A. L. Henne, and M. W. Renoll.[72] Using a carefully controlled fractional precipitation method, they obtained a series of products whose nitrogen contents increased as their solubility decreased. Although the initial material was completely soluble, they obtained finally an insoluble residue containing 4·21% of nitrogen. Similar results were obtained in the very careful work of G. F. Bloomfield and E. H. Farmer.[73] By repeated extractions with acetone–light petroleum mixtures of increasing petroleum content, they concentrated the bulk of the nitrogen in a residue of greatly reduced solubility. Their earlier fractions were, however, substantially nitrogen free, and it was shown [74] that the molecular weights of these fractions were related to the composition of the extractant by an equation of the form (25). Kemp and Peters [69] employed the other method of separation, and obtained by diffusion into hexane a series of fractions of increasing molecular weight. Later [70] they were able to extract small quantities of very low molecular-weight material by using hexane–acetone mixtures as extractant. A further complication is revealed when the most soluble fractions of rubber are examined. K. C. Roberts [75] and Bloomfield and Farmer [73] obtained materials of molecular weight 30,000—60,000 which contained 1—3% of oxygen. Roberts called his product "caoutchol" and showed that it possessed some extremely interesting physical properties, which have not yet been fully explained.

It will be evident that the solubility behaviour of rubber is far more complex than would be explicable by the idealised picture of it which forms the basis of the theoretical treatment, and little progress has yet been made in the application of these ideas to rubber. This is due in part to the experimental difficulties arising both from the protein content and from the ready oxidisability of rubber, and in part to the use of much too high concentrations in most of the attempted fractionations of rubber. It must be concluded that nothing approaching a complete fractionation of rubber has yet been achieved, and the evidence that a considerable proportion of rubber is reasonably homogeneous [72, 73] is almost certainly spurious.

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[72] *J. Amer. Chem. Soc.*, 1931, **53**, 2733; 1932, **54**, 3343.

[73] *Trans. Inst. Rubber Ind.*, 1940, **16**, 69.

[74] Gee and Treloar, *ibid.*, 1941, **17**, 184.

[75] *J.*, 1938, 215; 1942, 223.

Limited Swelling.

Closely related to the problem of solubility is that of swelling. When a soluble, high-molecular rubber is covered with solvent, it rapidly imbibes the solvent, increasing in volume without (in the early stages) much change of form. After a time, dispersion slowly takes place and a solution is produced. The phenomenon affords a visual indication of the difficulty of dispersing long-chain materials : the rate of diffusion of solvent into the rubber greatly exceeds that of the rubber outwards. If the liquid employed is a non-solvent, or the rubber is vulcanised, dissolution does not occur, but the rubber swells to a more or less well-defined equilibrium size. In measurements carried out in air, a definite limit is seldom observed, an initial rapid swelling being succeeded by a relatively slow absorption which continues indefinitely. The second stage, termed the " increment " by J. R. Scott,[76] is absent when oxygen is carefully excluded,[77] and should evidently be neglected in calculating the true equilibrium swelling.

The literature records an enormous number of swelling measurements, but their unsystematic nature renders many of them valueless from a scientific point of view. Whitby, Evans, and Pasternack [60] have provided data for a large range of liquids on the same rubber, and their work forms a useful basis on which to build or test any theory of swelling. These authors have drawn from their figures a number of interesting generalisations. Hydrocarbons in general are good swelling agents, the swelling being greatly diminished by the presence of a polar group, especially OH or CN. The effect of a given group is greatly diminished by a long hydrocarbon chain, and is less in aromatic compounds than in aliphatic. Addition of chlorine to the molecule usually enhances swelling.

A completely satisfactory theory of swelling should account quantitatively for these measurements : we are at present very far from such a state. The first attempt at a quantitative theory was made by Wo. Ostwald,[78] who proposed a relationship between the swelling Q (c.c. of liquid per c.c. of rubber) and the dielectric constant ε of the liquid, *viz.*,

$$Q = K\varepsilon^{-2 \cdot 16} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Accumulation of more data soon revealed the inadequacy of this expression, and it was later suggested [79] that swelling was a function of μ^2/ε and the surface tension σ, μ being the dipole moment. These two quantities have been combined by M. Takei [80] into the single parameter $\mu^2/\sigma\varepsilon$. There seems, however, little justification, either theoretical or experimental, for these suggestions.

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[76] *Trans. Inst. Rubber Ind.*, 1929, **5**, 95.

[77] Gee, unpublished experiments.

[78] *Kolloid-Z.*, 1921, **29**, 100.

[79] Ostwald, *J. Oil Col. Chem. Assoc.*, 1939, **22**, 31.

[80] *Kolloid-Z.*, 1942, **98**, 312.

The thermodynamic criterion for equilibrium swelling is given, of course, by $\Delta G_0 = 0$, or $\Delta H_0 = T\Delta S_0$. For raw rubber we may express ΔS_0 in terms of composition by one of the theoretical equations, or may take the measured values for benzene. The entropy of swelling of vulcanised rubber has not been measured, but will clearly be lower than that of raw, since cross linking reduces the number of possible configurations of the molecule. This effect will depend on the degree of vulcanisation, and will probably be important only at fairly high degrees of swelling. A semi-empirical method of deducing ΔS_0, for the vulcanisate used by Whitby and his co-workers, was suggested by Gee.[36] If we then write $\Delta H_0 \simeq k_0 v_r^2$, the equilibrium condition becomes

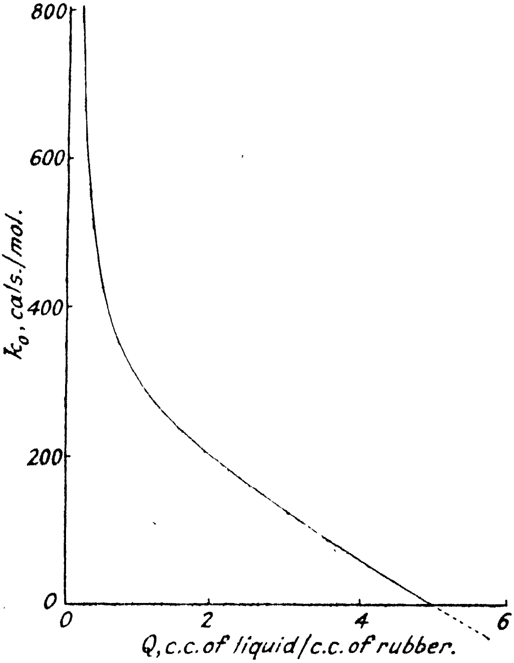

FIG. 4.

Relation between Heat and Extent of Swelling of Vulcanised Rubber.

$$T\Delta S_0/v_r^2 \simeq k_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

where the left-hand side is assumed to be the same for all liquids (though dependent on the state of vulcanisation of the rubber), and k_0 is a constant characteristic of the liquid. The function $T\Delta S_0/v_r^2$ becomes infinite at $v_r = 1$, and decreases continuously to zero at $v_r = p$, say, thereafter becoming negative. The swelling Q is, of course, $Q = (1 - v_r)/v_r$, and is therefore a function of k_0, which we can easily evaluate from equation (36). The curve resulting from Gee's estimate of the entropy of swelling is shown in Fig. 4. We have now to consider whether k_0 can be related to any other property of the liquid, and for this purpose we assume the relationship derived for simple liquids by J. H. Hildebrand [81] and G. Scatchard.[82] If E_0 and E_1 are the molar cohesive energies of the liquids, and V_0 and V_1 their molar volumes, we have

$$k_0 = \alpha V_0\{\sqrt{E_0/V_0} - \sqrt{E_1/V_1}\}^2 \quad . \quad . \quad . \quad . \quad (37)$$

Applied to rubber, this requires us to know the cohesive energy density E_1/V_1 of rubber, and Gee has shown that a value of 66 cals./c.c. leads to values of k_0 consistent with Whitby's swelling measurements. Equation (37) does not admit the possibility of negative values of k_0, and these are indeed to be ascribed always to specific interactions between the rubber and the liquid. Such cases being neglected, it is evident that $k_0 = 0$ when $E_0/V_0 = 66$, *i.e.*, rubber will swell to its maximum extent in a solvent whose cohesive energy density is 66 cals./c.c. This is very close to the value (66·54) for *cyclo*hexane.[83] Values of E_0/V_0 either higher or lower than 66 cals./c.c. will give positive values of k_0 and therefore lower values of Q. Hence, if we plot Q as a function of $x = \sqrt{V_0}\{\sqrt{E_0/V_0} - \sqrt{66}\}$, we should obtain a curve approximating in form to the error function, with its maximum at $x = 0$. Gee [36] has shown this to be roughly true, with certain well-defined exceptions. In the first place, aromatic and aliphatic liquids fall on separate curves, characterised by different values of α in equation (37) : this has not been satisfactorily explained. Highly associated liquids (alcohols, acids) give much too large Q values, showing the heat of swelling to be smaller than calculated. This is parallel to their behaviour in admixture with low-molecular hydrocarbons.[84] Chlorinated liquids also give unduly high values of Q. This again is readily explicable by analogy with simple liquid systems, for their heats of mixing with hydrocarbons are generally small and frequently negative.[85] Although, then, the above theory is believed to give a sound basis for the understanding of swelling, yet it is clear that exceptions to the generalisation will be frequent and may well be of great practical importance. Their elucidation, except in the above very crude way, has scarcely begun.

This review of the physical chemistry of rubber solutions reveals a field of work burdened with a mass of data which until recently were almost uncorrelated and imperfectly understood. Considerable theoretical advances have been made in the last few years, and provide a sound foundation on which to build, but we have a long way to go yet before anything approaching a complete understanding is achieved.

G. G.

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[81] *Op. cit.*, p. 73.
[82] *Chem. Reviews*, 1931, **8**, 321; *J. Amer. Chem. Soc.*, 1934, **56**, 995.
[83] H. Scatchard, S. E. Wood, and J. M. Mockel, *J. Physical Chem.*, 1939, **43**, 119.
[84] K. L. Wolf, H. Pahlke, and K. Wehage, *Z. physikal. Chem.*, 1935, *B*, **28**, 1.
[85] "International Critical Tables," Vol. 5, pp. 150 *et seq.*

3. THE ATOMIC REACTIONS OF THE ALKALI METALS.

In the development of the theory of chemical reactivity the natural starting point was the investigation of the simplest type of reaction, that of a free atom with a molecule. Such reactions require the rupture of the minimum number of bonds and on this account should be more readily amenable to theoretical treatment. Furthermore, a systematic experimental and theoretical examination of atomic reactions would lead to the discovery of a clear-cut set of rules which would provide a basis for the understanding of more complex reactions. In this respect, the reaction of the alkali-metal atoms with the halogens, hydrogen halides, metallic halides, organic halogen compounds, and in a few cases, compounds containing oxygen and sulphur, which have been carried out almost entirely by M. Polanyi and his collaborators over the last 18 years, provides one of the most complete chapters in reaction kinetics. In the present Report the experimental and theoretical data relating to this work have been summarised.

Since many atomic reactions of the alkali metals occur at far greater velocities than can be measured by ordinary methods, it was found necessary to devise new methods suitable for the direct measurements of the rate of fast reactions. Of these, the method of highly dilute flames (so-called because the reactions studied in this way were chemiluminescent) was suitable only for reactions which occur at almost every collision. The second method, called " the diffusion method," which eliminates the possibility of surface reaction, can be used for reactions occurring slower than every tenth (or possibly fifth), or faster than every hundred-thousandth collision of the reaction partners. The third, and most recently developed, method—" the life-period method "—is of wide application and more reliable than the diffusion method. The majority of the investigations have been carried out by the first two methods.[1] Since there is a fairly sharp distinction between the type of reaction studied by these methods, the results have been summarised according to the method of investigation employed.

I. *Highly Dilute Flames.*

This method was developed by H. Beutler and M. Polanyi [2] for the measurement of reactions occurring at every collision. In this method, the vapour streams of the reacting substances, *e.g.*, sodium and halogen, enter at opposite ends of an evacuated tube and at a pressure (10^{-3} mm.) such that the mean free path is greater than the diameter of the tube. Under these conditions the reaction zone (" flame," since the reaction is accompanied by luminescence) is several cm. in length, and it is possible to measure with accuracy the density of the distribution both of the solid product deposited on the walls of the tube and of the chemiluminescence produced. The extent of the reaction will be greatest at the centre of the reaction zone where most penetration has occurred, and will decrease on both sides. If, therefore, no secondary reactions interfere, the precipitation curve will be symmetrically bell shaped. It is at once apparent that the slower the reaction velocity the greater the zone of penetration and the broader the deposit curve. By expressing the condition of the stationary state—namely, that the amount of reactant consumed by reaction in any element of volume is equal to the quantity of that reactant accumulating there by diffusion—in terms of a differential equation, and integrating, an expression was obtained which gave the reaction velocity constant, k, directly in terms of the measured half-breadth of the precipitation curve and the tube resistances of the reacting partners.

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[1] A detailed review of the work on " Highly dilute flames " is given by G. Schay (*Fortschr. Chem. Physik und physikal. Chem.*, 1931, **21**). An excellent general review of both the " highly dilute flame " and the " diffusion flame " method may be found in the monograph by M. Polanyi, "Atomic Reactions," Williams and Norgate, 1932.

[2] *Naturwiss.*, 1925, **13**, 711; *Z. Physik*, 1928, 47, 379; *Z. physikal. Chem.*, 1928, *B*, **1**, 3.

This method was employed in investigating the reactions of sodium and potassium with chlorine,[3] bromine,[4] iodine,[5] and volatile halides;[6] the resulting halides of the metals are non-volatile and readily retained by the walls of the reaction vessel. All of these reactions were accompanied by a strong luminescence, the investigation of which proved to be extremely important in the elucidation of the mechanisms of the reactions occurring. The luminescence in the case of sodium vapour reactions resulted from the chemical excitation of the D line.[7] Haber and Zisch, who had previously observed this emission in the reaction of sodium vapour with halogen and halogen compounds in nitrogen at atmospheric pressure, explained it as arising from the collisions of the molecules formed in the reaction and carrying most of the energy liberated in the reaction with sodium atoms and exciting the latter. At low pressures the light was of much greater intensity, and it was this particular property that gave rise to the name "highly dilute flames."

A detailed examination of the luminescence was carried out by St. v. Bogdandy and M. Polanyi [8] by the use of a "nozzle flame." The halogen was introduced from a nozzle into an excess of sodium vapour, and the luminescence was thus rendered much more intense. It was observed that the light-distribution curve did not coincide with the precipitate-distribution curve, and this was explained by the occurrence of the reaction in two stages, the primary reaction

$$\mathrm{Na} + \mathrm{Cl}_2 \longrightarrow \mathrm{NaCl} + \mathrm{Cl} + 40{\cdot}7\ \text{kg.-cals.} \quad \ldots \quad (1)$$

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[3] M. Polanyi and G. Schay, *Z. physikal. Chem.*, 1928, *B*, **1**, 30, 384.

[4] H. Ootuka, *ibid.*, 1930, *B*, **7**, 406. [5] H. Ootuka and G. Schay, *ibid.*, 1928, *B*, **1**, 62.

[6] *Idem, ibid.*, p. 68 (Na + $HgCl_2$); see Ref. (4) (Na + $HgBr_2$).

[7] F. Haber and W. Zisch, *Z. Physik*, 1922, **9**, 302; H. Franz and H. Kallman, *ibid.*, 1925, **34**, 924; K. Liakilov and A. Terenin, *Naturwiss.*, 1926, **14**, 83; H. Beutler, St. v. Bogdandy, and M. Polanyi, *Z. Physik*, 1928, **47**, 379; H. Beutler and B. Josephy, *Naturwiss.*, 1927, **15**, 540; R. L. Hasche, M. Polanyi, and E. Vogt, *Z. Physik*, 1927, **41**, 583; K. Kondratjew, *ibid.*, 1927, **45**, 67; 1928, **48**, 310.

[8] *Z. physikal. Chem.*, 1928, *B*, **1**, 21. The heats of reaction given in this Report were calculated from the most recent values of the heats of dissociation of Na_2, Cl_2, and NaCl, *viz.*, 17·5, 56·8, and 97·5 kg.-cals., respectively, and differ from the values in the original papers by 5—10 kg.-cals.

which took place entirely in the gas phase, and a secondary reaction of the chlorine atoms formed with the portion of the sodium present as molecules:

$$Cl + Na_2 \longrightarrow NaCl^* + Na + 80 \text{ kg.-cals.} \quad . \quad . \quad . \quad (2)$$

Most of the chlorine atoms, however, disappeared by reaction on the walls of the tube,

$$Na + Cl \longrightarrow NaCl + 97{\cdot}5 \text{ kg.-cals. (wall reaction)} \quad . \quad . \quad (3)$$

It was established that the secondary reaction involved Na_2 molecules by the following observations: (*a*) The intensity of the light was diminished and almost completely extinguished by raising the temperature of the reaction zone; this was quantitatively explained by the increased dissociation of the Na_2 molecules at the higher temperature. (*b*) The light yield increased with sodium pressure more rapidly than would correspond to a linear relationship. These observations may be completely explained on the basis that the light was produced, not by direct excitation of the sodium atoms produced in (2), but by collision of the $NaCl^*$ molecules (carrying most of the energy of the reaction) with other sodium atoms which were thereby excited to emission of the D line:

$$NaCl^* + Na \longrightarrow NaCl + Na^* (^2P) \quad . \quad . \quad . \quad . \quad (4)$$

$$Na^* \longrightarrow Na + h\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This view was confirmed by quantitative measurements on the quenching of the luminescence by added nitrogen.[3] According to this mechanism, both the secondary and the wall reaction contribute towards the total deposit of halide, and so the velocity constant could not be determined directly from the half-breadth of the precipitation curve. However, from a quantitative analysis of the precipitation- and light-distribution curves, it was possible to resolve the deposit into its part reactions and so to determine accurately the velocity constants of the primary, secondary, and wall reactions for the reaction of sodium vapour with chlorine, bromine, and iodine. It was found that all the gas reactions occur without activation energy, some of the reactions, in fact, occurring at a greater rate than that calculated on the normal kinetic theory basis if every collision is assumed to be effective. It was shown by St. v. Bogdandy and M. Polanyi[9] that when sodium atoms are introduced into a mixture of chlorine and hydrogen, several thousand molecules of hydrogen chloride are formed for each alkali atom reacting. This confirms the occurrence of the primary reaction (1), the split-off chlorine atom inducing the H_2–Cl_2 chain. This inducing effect can also be demonstrated in a mixture of chlorine and methane, *e.g.*,

$$\begin{aligned} Na + Cl_2 &\longrightarrow NaCl + Cl \\ Cl + CH_4 &\longrightarrow HCl + CH_3 \\ CH_3 + Cl_2 &\longrightarrow CH_3Cl + Cl, \text{ etc.} \end{aligned}$$

Similar investigations have been carried out with potassium vapour and the halogens. H. Ootuka[10] used potassium containing 7% of sodium in order to permit visual observation of the luminescence, since the violet radiation of potassium is poorly visible. M. Kroosak and G. Schay[11] and F. Roth and G. Schay[12] worked with pure potassium and showed that the reactions occurred with zero activation energy by a similar mechanism to that of sodium, but the chemiluminescence was much more complicated. The reactions of both sodium and potassium with the hydrogen halides were investigated by G. Schay,[13] using the " nozzle flame method." In both cases the reaction velocity increased from hydrogen chloride to hydrogen iodide, and this was in the order of the heats of reaction of the different series. In those cases where the heats of reaction were positive it was found that, to account for the observed velocities, enhanced collision diameters had to be introduced into the gas kinetic expression. The chemiluminescence of these reactions probably occurs by a secondary reaction of hydrogen atoms produced in the primary reaction, *viz.*, $Na + ClH \longrightarrow NaCl + H - 5000$ cals., although the actual fate of the hydrogen atoms is not certain.

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[9] *Z. Elektrochem.*, 1927, **33**, 554; *Naturwiss.*, 1927, **15**, 40; M. Polanyi, *Trans. Faraday Soc.*, 1928, **24**, 606.

A further group of reactions of which the mechanism has been investigated by the method of highly attenuated flames is that of the volatile inorganic halides of mercury,[14] cadmium and zinc[15] with both sodium and potassium vapour. The reaction mechanism was shown to be the following:

$$\text{Primary reaction: } Na + HgCl_2 \longrightarrow NaCl + HgCl + 25 \text{ kg.-cals.}$$
$$\text{Secondary reaction: } Na + HgCl \longrightarrow NaCl^* + Hg + 65{\cdot}3 \text{ kg.-cals.}$$
$$NaCl^* + Na \longrightarrow Na' + NaCl \longrightarrow Na + h\nu$$

The sole source of the luminescence, which was much weaker than in the case of the halogens, was found to be the secondary reaction. In contradistinction to the reactions of the halogens, all the phenomena connected with the presence of Na_2 molecules were absent, since no free halogen atom was produced in the primary reaction. All of these reactions occurred without inertia.

M. Polanyi and G. Schay[16] observed that when sodium vapour reacts with stannic chloride, bromide, or iodide, the light emission is different from that observed in the previous reactions and shows a completely continuous spectrum. This luminescence is of a primary character and is emitted during, and not subsequent to, the primary reaction. The explanation offered was that the $SnCl_3$ radicals formed by the reaction $Na + SnCl_4 \longrightarrow NaCl + SnCl_3$ lead to a subsequent luminescent reaction, $SnCl_3 + SnCl_3 \longrightarrow SnCl_2 + SnCl_4 + h\nu$. R. A. Ogg and M. Polanyi[17] have explained the mechanism of this emission in terms of their theory of ionogenic reactions. They consider that the newly-formed $Sn^{IV}Cl_2$ molecule passes over, by electronic transition accompanied by the emission of light, into the stable $Sn^{II}Cl_2$ molecule. The continuous nature of the emission is explained by variable quantities of energy being taken up by the translational motion of the two newly-formed molecules, which fly off in opposite directions (the inverse of the predissociation process).

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[10] *Z. physikal. Chem.*, 1930, *B*, **1**, 422.
[11] *Ibid.*, 1932, *B*, **19**, 344.
[12] *Ibid.*, 1935, *B*, **28**, 323.
[13] *Ibid.*, 1931, *B*, **11**, 291.

[14] H. Beutler, St. v. Bogdandy, and M. Polanyi, *Naturwiss.*, 1926, **14**, 164; also refs. (3) and(8); H. Ootuka and G. Schay, ref. (6); K. Kondratjew, *Physikal. Z. Sovietunion*, 1933, **4**, 57; J. Berger and G. Schay, *Z. physikal. Chem.*, 1935, *B*, **28**, 332; H. Ootuka, *ibid.*, 1930, *B*, **7**, 406.

[15] E. Horn, M. Polanyi, and H. Sattler, *ibid.*, 1932, *B*, **17**, 220.

[16] *Z. Physik*, 1928, **47**, 814.

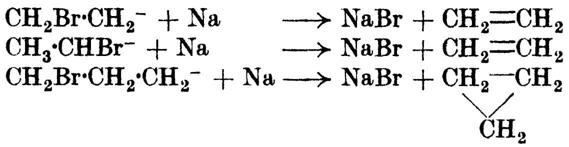
[17] *Trans. Faraday Soc.*, 1935, **31**, 1375.

No luminescence was observed in the reaction of the organic monohalogen compounds, but when the number of halogen atoms in the organic molecule was increased, an intense luminescence of the D line of sodium was produced. For instance, all the saturated dihalides [18] so far examined have shown this characteristic luminescence. The light is produced homogeneously, and the reaction was shown to occur in two stages, corresponding to the successive removal of the halogen atoms :

$$RX_2 + Na \longrightarrow NaX + \cdot RX \quad . \quad . \quad . \quad . \quad (1)$$

$$\cdot RX + Na \longrightarrow (R) + NaX \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the product R being a biradical, unsaturated molecule, or cyclic compound. Neither reaction (1) nor reaction (2), if R was a biradical, was sufficiently exothermic to lead to the excitation of the D line. Experimental data also showed that no reactions involving Na_2 molecules gave rise to sufficient energy. It was concluded that the excitation reaction was the exothermic rearrangement of R. These reactions were of two types according to whether (*a*) R is an unsaturated molecule formed either by the closure of a double bond or by migration of a hydrogen atom, or (*b*) R is a cyclic molecule. These classes of reaction are typified by ethylene dibromide, ethylidene dibromide, and trimethylene bromide :



$$CH_2Br\cdot CH_2^- + Na \longrightarrow NaBr + CH_2{=}CH_2$$
$$CH_3\cdot CHBr^- + Na \longrightarrow NaBr + CH_2{=}CH_2$$
$$CH_2Br\cdot CH_2\cdot CH_2^- + Na \longrightarrow NaBr + \underset{\diagdown\,CH_2\,\diagup}{CH_2{-}CH_2}$$

By analogy with the halogen reactions, it was assumed that the sodium halide formed possesses an internal energy greater than 50 kg.-cals., which is transferred to the sodium atom by collision, thus leading to luminescence.

In the case of methylene bromide or iodide, the necessary energy for excitation is supplied by the change in valency of the carbon atom in passing from the quadrivalent to the bivalent state in methylene. This change in valency of the carbon also explains the luminescence of the reactions of the polyhalogen methane derivatives studied by Haresnape, Stevels, and Warhurst (p. 42).

II. *Diffusion Flames.*

The method of highly dilute flames is not suitable for reactions which do not occur at approximately every collision, since in such cases the length of the tube needs to be very great. The method also suffers from the further disadvantage that unless the reaction is accompanied by luminescence it is very difficult to estimate the part played by wall reactions. These difficulties are avoided in the " diffusion flame " method developed by H. v. Hartel and M. Polanyi.[19] The principle of the method is similar to that of the nozzle flames in that it measures the distance one component can diffuse into the other before being consumed by reaction, but by introducing both reactants in a stream of inert gas, diffusion can be made so slow that the sodium vapour leaving the nozzle is used up before reaching the walls. Surface reactions are thereby eliminated. The distance to which the sodium vapour penetrates is observed by means of a resonance lamp. By setting up the conditions of the stationary state and integrating, the following simple formula for the velocity constant, k, may be deduced,[19]

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[18] C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, 1939, **35**, 185.

$$k = (\delta/r^2 p_{\mathrm{HI}}) \ln (p_T/p_0)^2$$

where p_0 and p_T are respectively the pressures of sodium at the nozzle and the edge of the " sodium flame "—made visible by the resonance light, r is the radius of the flame, δ the diffusion constant of sodium, and p_{HI} the pressure of halide in the reaction vessel. The derivation of this formula depends, however, on the validity of several assumptions which in the earlier work may not have been strictly fulfilled. An elaborate investigation of these assumptions was subsequently carried out by W. Heller,[20] who determined the conditions under which the above formula holds good, and under which the method may be employed to give quantitative determinations of reaction velocities. By the use of the original method, v. Hartel and Polanyi [19] and H. v. Hartel, N. Meer, and M. Polanyi [21] carried out a systematic investigation of the reactivity of organic halides towards atomic sodium. It is not possible in this review to give more than a general summary of their results, any reference to the particular organic halides investigated being omitted. The authors showed that an increase in rate of reaction was produced by the following factors : (*a*) Variation of halogen from fluorine to iodine in the methyl, ethyl, and phenyl halides. (*b*) Lengthening of the hydrocarbon chain, R, in the series RCl. (*c*) Passage from primary to secondary to tertiary carbon. (*d*) Introduction of double bonds or carbonyl groups in neighbouring positions to the halogen. (*e*) Multiple substitution by halogens; the greater effect was obtained when the chlorine atoms in the molecule were closer together, and a retardation of the reaction was observed when the chlorine atom was attached to a doubly-bound carbon atom.

The laws deduced were explicit and simple, and N. Meer and M. Polanyi [22] showed that there was a remarkable parallelism between the sodium atom reactions and organic reactions in which a single ion reacts with a molecule, *e.g.*, $I^- + CH_3Cl \longrightarrow CH_3I + Cl^-$. The parallelism was not complete, and in some cases an inverse effect was observed in the two groups, *e.g.*, the effect of increase in chain length. These differences, however, were explained on theoretical grounds. As a whole, the results achieved in this work must be regarded as a most valuable contribution to the elucidation of the mechanism of organic reactions.

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[19] *Z. physikal. Chem.*, 1930, *B*, **11**, 97.

[20] *Trans. Faraday Soc.*, 1937, **33**, 1556.

[21] *Z. physikal. Chem.*, 1932, *B*, **19**, 139.

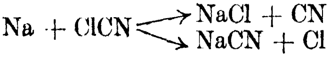
[22] *Ibid.*, p. 164.

More recently, J. N. Haresnape, J. M. Stevels, and E. Warhurst [23] have compared the reaction velocities of eleven of the fourteen possible methane derivatives containing chlorine or bromine or both. The authors conclude that an increase in atomic refraction runs parallel with a decrease in collision number. W. Heller and M. Polanyi [24] had previously pointed out the parallelism between decreasing force constants of the C–Cl linkage and increasing rate of reaction in the series, $CH_3Cl \longrightarrow CCl_4$.

The velocities of the reaction of sodium with the hydrogen halides has been determined by H. v. Hartel.[25] The same order of reactivity was observed as that found by Schay (*loc. cit.*), using the highly dilute flame technique. More recently, C. E. H. Bawn and A. G. Evans [26] have shown that the rates of reactions of hydrogen and deuterium chloride are approximately the same, the activation energies being 6100 and 6400 cals., respectively. It is of interest that the full zero-point energy differences of HCl and DCl ($\sim$ 1500 cals.) do not appear in the differences of activation energy. The reasons for this have been discussed theoretically by A. G. Evans and M. G. Evans.[27]

The reaction of sodium with cyanogen gas [19] differs in a characteristic manner from that of the halogens in that the reaction $Na + (CN)_2 \longrightarrow NaCN + CN$, although exothermic, occurs at 1 in 15,000 collisions and the collision yield is the same at 300° and 500°. The inertia is thus not the result of an activation energy factor but is probably due to steric hindrance.

The reaction with cyanogen chloride and cyanogen bromide [28] was followed by determining of the ratio of the products NaCl (or NaBr) and NaCN. The ratio of these products, formed in the primary reaction, was not greater than 1 : 50 and decreased with increase in temperature. The results can be explained by the occurrence of two primary reactions :



$$Na + ClCN \begin{cases} \longrightarrow NaCl + CN \\ \longrightarrow NaCN + Cl \end{cases}$$

which take place at different rates. The mechanism of the luminescence of these reactions is similar to that of the halogens.

The reaction velocities of a series of inorganic polyhalides (BCl_3, BBr_3, CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$, PCl_3, $AsCl_3$, SCl_2, S_2Cl_2, $COCl_2$, $POCl_3$, and CrO_2Cl_2) have been determined, by means of the diffusion-flame technique, by W. Heller and M. Polanyi,[29] who concluded, from these and previous investigations on the halides of the second period, that the polyhalides of the elements belonging to the middle groups of the periodic table show the highest inertia in their reactions with sodium vapour. With each of the series, $CCl_4 \longrightarrow SnCl_4$, $CH_3Cl \longrightarrow CCl_4$, and $CH_3Cl \longrightarrow CH_3I$, the chemical inertia was shown to increase with increase of the restoring force acting in the halogen linkage. Visible luminescences were obtained with all the above compounds with the exception of $SiCl_4$ and $AsCl_3$. The luminescences of $COCl_2$ and PCl_3 reactions were identified as the sodium D line and probably arise by a mechanism similar to that of the halogens or mercuric halides (*loc. cit.*). The luminescence observed with $GeCl_4$ and the other compounds investigated, with the exceptions of $COCl_2$, PCl_3, CCl_4, $SiCl_4$, and $AsCl_3$, showed a continuous spectrum similar to that with $SnCl_4$ (*loc. cit.*) and may be accounted for by a mechanism similar to that given for the latter. In the reactions of S_2Cl_2, SCl_2, or CS_2, a further series of luminescences was observed when oxygen was added, and although no explanation of this was given, it should be noted that sulphur was present in each of the molecules.

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[23] *Trans. Faraday Soc.*, 1940, **36**, 465.

[24] *Compt. rend.*, 1934, **199**, 1118; W. Heller, *ibid.*, p. 1611.

[25] *Z. physikal. Chem.*, 1931, *B*, **11**, 316.

[26] *Trans. Faraday Soc.*, 1935, **31**, 1392. [27] *Ibid.*, p. 1400.

[28] J. Curry and M. Polanyi, *Z. physikal. Chem.*, 1932, *B*, **20**, 276; see also ref. (19).

[29] *Trans. Faraday Soc.*, 1936, **32**, 633.

The modified procedure of W. Heller and M. Polanyi [29] has been used by C. E. H. Bawn and A. G. Evans [30] for measurement of the velocity of reaction of sodium atoms with oxygen, the oxides of nitrogen and sulphur, and with nitromethane, ethyl nitrate, and amyl nitrite. These studies present a new feature in so far as the attack of the sodium was at a multivalent atom. The reaction between sodium and oxygen was first investigated by the diffusion flame method by F. Haber and H. Sachse,[31] who showed that the velocity constant varied linearly with the inert-gas pressure. They interpreted these results in terms of the termolecular reaction, $Na + O_2 + X \longrightarrow NaO_2 + X$, where the inert gas X acts as a third body to carry off the energy of the reaction. Bawn and Evans confirmed these observations at low inert-gas pressures, but found that at higher carrier-gas pressures the reaction changes over to a simple bimolecular association process. The following mechanism was suggested :

$$\begin{array}{lll} Na + O_2 & \longrightarrow NaO_2^* & (k_1) \\ NaO_2^* & \longrightarrow Na + O_2 & (k_2) \\ NaO_2^* + X & \longrightarrow NaO_2 + X & (k_3) \end{array}$$

where X is the inert gas and the asterisk indicates that the molecule possesses the heat of reaction as internal energy. By setting up the conditions of the stationary state it was shown that

$$-\, dp_{Na}/dt = kp_{Na}p_{O_2} = k_1k_3p_Xp_{Na}p_{O_2}/(k_2 + k_3p_X)$$

where k is the measured velocity constant, calculated from the expression given on p. 41, whence it follows that

$$k = k_1k_3p_X/(k_2 + k_3p_X)$$

and at high pressures, when $k_2 \ll k_3$, $k = k_1$, *i.e.*, the reaction is bimolecular. The values of k_1, k_2, and k_3 were determined from the experimental data for both the reactions of oxygen and nitric oxide. The lifetime of the intermediate complex, τ $(= 1/k_2)$, was found to be about 10^{-9} sec. for both NaO_2^*

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[30] *Trans. Faraday Soc.*, 1937, **33**, 1580.

[31] *Z. physikal. Chem.*, Bodenstein Festband, 1931, **831**.

and NaNO*. The values of k_1 were 10^2 to 10^3 times smaller than those calculated by the kinetic theory expression, and this was shown to be due to a transition probability consequent on a change of multiplicity of state, which appeared as a steric factor in the reaction velocity expression.

Hydrogen sulphide was found to react with sodium at about the same rate as nitric oxide, and preliminary observations showed that the rate depended on carrier-gas pressure, as with oxygen and nitric oxide. W. Heller and M. Polanyi[29] observed that carbon disulphide reacted slowly with sodium atoms and interpreted their result in terms of a three-body collision mechanism. Both sulphur di- and tri-oxide showed remarkable reactivity towards sodium, the collision efficiency being about 1/10. Thermochemical considerations indicate that none of the above reactions could proceed under the conditions of the experiments by a metathesis reaction, and it was concluded therefore that all were association reactions. In the reactions of the sulphur oxides, association occurred at every collision, the lifetime of the intermediate complex being sufficiently long to ensure that it experienced at least one collision with an inert-gas molecule during its lifetime. Sodium atoms were found to be unreactive towards water vapour and carbon dioxide at inert-gas pressures from 2 to 13 mm.

The reactions of sodium with nitrous oxide and nitrogen dioxide[30] take place according to a bimolecular law, with collision numbers of 40 and 10 respectively. Both reactions are accompanied by an intense luminescence of the sodium D line, and this was explained by the occurrence of a series of reactions analogous to those of the halogens, *viz.*,

$$Na + N_2O \longrightarrow N_2 + NaO \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

$$NaO + Na_2 \longrightarrow Na_2O^* + Na \quad . \ . \ . \ . \ . \ . \ . \quad (2)$$

$$Na_2O^* + Na \longrightarrow Na_2O + Na^* \longrightarrow Na + h\nu \quad . \ . \quad (3)$$

The mechanism was in agreement with the observations that (*a*) the luminescence decreased with increase in temperature of the reaction zone, (*b*) the greatest luminescence was in the region of the nozzle, where the concentration of Na_2 molecules was highest, (*c*) neither (1) nor (4) was sufficiently

$$Na + NO_2 \longrightarrow NaO + NO \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

exothermic to allow of the production of luminescence in the primary reaction.

In contrast to the alkyl halides, the variation of structure from nitromethane to ethyl nitrite to amyl nitrite[32] caused no appreciable change in the activation energy, which in each case was about 2500 cals.

III. *Life-period Method.*

The " diffusion flame " method, although free from the difficulties of wall reaction, relied for the evaluation of the reaction velocity constant on calculations of a somewhat doubtful degree of approximation, concerning the stationary distribution of a diffusing and at the same time reacting gas.

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[32] C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.*, 1937, **33**, 1571.

Following a critical examination of the possible errors, W. Heller[20] has ascertained the experimental conditions under which the measured reaction velocity should not differ by more than a factor of 2 from the absolute rates for reactions with collision numbers between 50 and 5000. By a further modification of the conditions, and using hydrogen as carrier gas, J. N. Haresnape, J. M. Stevels, and E. Warhurst[23] have extended the diffusion flame method to reactions with collision yields of 10 or possibly less. A new method has, however, been developed by L. Frommer and M. Polanyi[33] which embodies the main experimental feature of the diffusion method but is based upon a different set of measurements which leads to the evaluation of the velocity constant independently of any assumptions as to the spatial distribution of the gases in the flame. The new method can be used over a wider range of velocities and reacting substances than the diffusion method. The principle of the method of measurement is as follows : A known stream of n atoms of sodium vapour is introduced into the reaction chamber containing an excess concentration c of the halogen compound, and the number N of sodium atoms in the stationary reaction zone (" flame ") is measured. The amount of reaction occurring in any element of volume, dv, per sec. is $kncdv$. If c is kept uniform over the reaction zone, the total reaction is $kc\int ndv$. The $\int ndv$ is the number of atoms, N, present in the reaction zone in the stationary state. Since the total amount of reaction is equal to n, and all atoms entering the reaction zone are consumed before reaching the wall, it follows that $n = kcN$ or $k = 1/\tau c$ since $\tau = N/n$ = average life of the sodium atom in the reaction vessel. Both n and c can be evaluated from the measured rate of flow of sodium and halogen compound into the reaction vessel, and the number of sodium atoms in the uncombined state can be determined by measuring the absorption of resonance radiation of sodium vapour passed through the flame. In the initial investigations, the latter was determined by photographic measurements, but this laborious method has been replaced by a sensitive photoelectric photometer which measures the intensity of the light beam directly.[34]

A comparison, in the case of methyl bromide, with the published measurements of Hartel and Polanyi,[19] who used the diffusion method, showed a marked difference. There was, however, a close correspondence with the results obtained by the revised diffusion method of W. Heller and M. Polanyi.[24] This was further substantiated by the fairly extensive comparison of the reactivities of the polyhalogenated methanes which have been measured by the life-period and the revised diffusion-flame method.[23]

The new method has been employed by F. Fairbrother and E. Warhurst[35] in the reactions of sodium vapour with chloro-, bromo-, and iodo-benzene. They find that the reaction rates increase in the above order, and that the effect of change of halogen is much the same in the benzene series as in the case of the corresponding methyl compounds. E. Warhurst[36] has recently carried out a more detailed investigation of the bromobenzene reaction in order to define more closely the conditions under which the most reliable values for the velocity constant may be obtained.

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[33] *Trans. Faraday Soc.*, 1934, **30**, 519.

[34] F. Fairbrother and F. L. Tuck, *ibid.*, 1936, **32**, 624.

[35] *Ibid.*, 1935, **31**, 987.

[36] *Ibid.*, 1939, **35**, 674.

The Formation of Radicals by the Interaction of Sodium Vapour and Organic Halides.—Much evidence has accumulated to show that the primary reaction of sodium atoms with organic halides, $RX + Na \longrightarrow NaX + R-$, results in the liberation of free radicals. For instance, by introducing the products of the reaction of sodium with methyl bromide into chlorine or iodine, E. Horn, M. Polanyi, and D. W. G. Style [37] showed that bromo- and iodo-methane were formed. Similar experiments were carried out with ethyl [37] and phenyl [38] radicals. Additional support for this conclusion was obtained when the CH_3Br–Na reaction was carried out in the presence of hydrogen. Thus, H. v. Hartel and M. Polanyi [39] found that two molecules of methane were formed for each hydrogen molecule consumed. In the absence of hydrogen, the product was ethane formed by the dimerisation of the methyl radicals. In the same way the products of the reaction of chlorobenzene,[40] benzoyl chloride and acetonyl chloride [41] have been identified as their dimers. A conclusive proof of the formation of free radicals in the reaction of sodium and bromomethane was provided by A. O. Allen and C. E. H. Bawn,[42] who showed that mirrors of tellurium and antimony were removed when placed at a considerable distance from the reaction zone. With tellurium the methyl derivative of the metal was isolated. The concentration of the radical removing the mirror was shown to fall off with the square of the distance from the mirror, showing that it must be formed in the reaction zone and diffuses outwards. The reaction of sodium with the aliphatic dihalides [43, 44] has been used to prepare and study the reactions of biradicals.

IV. *Theoretical.*

The reactions of the alkali-metal vapours with the halogens or halides form ionically bound molecules and belong to a large group of reactions termed by R. A. Ogg and M. Polanyi [45] "ionogenic," *i.e.*, they involve the transfer of electric charge—an atom bound initially by a homopolar linkage passes into the ionic state. If the alkali vapour–halogen reactions proceeded by means of a purely atomic process resulting in the formation of an atomically bound halide molecule (which eventually made a transition, with the loss of energy, to the ionic state), then they would be highly endothermic in the intermediate stage and hence would possess large activation energies. This is contrary to experimental fact, and hence the transition to the ionically bound halide molecule which renders the reaction energetically possible must occur whilst the reacting system is still in the intermediate configuration.

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[37] *Trans. Faraday Soc.*, 1934, **30**, 189.

[38] E. Horn and M. Polanyi, *Z. physikal. Chem.*, 1934, *B*, 25, 151.

[39] *Ibid.*, 1930, *B*, **11**, **97**; H. v. Hartel, *Trans. Faraday Soc.*, 1934, **30**, 187.

[40] *Idem, ibid.*

[41] J. N. Haresnape, Thesis, University of Manchester.

[42] *Trans. Faraday Soc.*, 1938, **34**, 463.

[43] C. E. H. Bawn and R. F. Hunter, *ibid.*, p. 608.

[44] C. E. H. Bawn and J. Milsted, *ibid.*, 1939, **35**, 889.

[45] *Mem. Manchester Lit. Phil. Soc.*, 1933–34, **78**, 41; *Trans. Faraday Soc.*, 1935, **31**, 1375.

A theory of these reactions was put forward by R. A. Ogg and M. Polanyi [45] which explains many of their fundamental features. The general form of the theory can be illustrated by considering a typical system,

$$\mathrm{Na} + \mathrm{ClR} \longrightarrow \mathrm{Na^+Cl^-} + \mathrm{R} \quad . \; . \; . \; . \; . \; (1)$$

On one side we have a homopolar state, and on the other an ionic state, and the method consists in calculating two energy surfaces corresponding respectively to these states. A linear configuration of the three interacting particles being assumed, both surfaces can be represented in terms of two co-ordinates, *viz.*, the separation (*a*) of sodium and chlorine atoms and (*b*) of the chlorine atom and the carbon atom of the radical R. Both of these surfaces are calculated by the use of appropriate potential-energy functions. The important features of these surfaces are the following : The three-atom, homopolar surface $(\mathrm{Na{-}Cl{-}R})_\mathrm{h}$ forms two valleys, representing the initial and the final state, between which lies a saddle. The final-state valley determined in this way corresponds to the homopolar molecule and the free radical R, and will not be the true final state. The latter is represented on the surface $(\mathrm{Na{-}Cl{-}R})_\mathrm{ionic}$, for which the NaCl is ionically bound. The energy of this valley lies below the final-state valley $(\mathrm{Na{-}Cl{-}R})_\mathrm{h}$. Conversely, there is a shallow valley representing the initial state of the ionic surface (in which the sodium ion is free and the chlorine ion loosely bound to R). Reaction (1) thus occurs by a transition from the initial-state valley of the surface $(\mathrm{Na} \ldots \mathrm{Cl} \ldots \mathrm{R})_\mathrm{h}$ to the final-state valley $(\mathrm{Na} \ldots \mathrm{Cl} \ldots \mathrm{R})_\mathrm{i}$. The two surfaces cross each other, and the line of intersection represents all possible transitions between the initial and the final state. The point of lowest energy value on this intersection line corresponds to the actual transition state, and the difference in energy between this state and the initial state gives the upper limit of the activation energy. However, on account of resonance between the two states, the surfaces never really cross but separate into two continuous energy surfaces. The question as to whether the reaction follows the lower of these two surfaces (adiabatic mechanism) or whether there is a probability of a transition across the gap between the surfaces (diabatic mechanism) has been frequently discussed.[46] The general conclusion has been reached that, for the above types of ionogenic reaction, the crossing point is a good approximation to the transition state and that there is no restriction on the passage from one surface to the other.

This theory has been applied to the calculation of the activation energies for the reaction of sodium vapour with (*a*) methyl and phenyl halides,[47]

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[46] M. G. Evans and E. Warhurst, *ibid.*, 1939, **35**, 593; H. London, *Z. Physik*, 1932, **74**, 143; R. A. Ogg and M. Polanyi, ref. (45); M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11; J. L. Magee, *J. Chem. Physics*, 1940, **8**, 687; E. Wigner, *Trans. Faraday Soc.*, 1938, **34**, 29.

[47] M. G. Evans and E. Warhurst, ref. (46).

(*b*) hydrogen and deuterium halides,[48] and (*c*) the alkali metals.[49] Evans and Polanyi [46] showed that in the reaction of sodium with the alkyl halides, repulsive forces were absent on one side of the reaction and that the sodium atom could approach the homopolarly bound halogen atom as far as the normal bonding distance of the ionic NaHal without incurring repulsion. This led to a very considerable simplication in the method of representing the changes occurring in terms of energy surfaces, and the activation energy could now be found without plotting energy surfaces. It may be deduced from the theoretical calculations that in the series RCl and Li, Na, K, etc., the change in activation energy should follow the heat of reaction, but in the series, RCl + Na, RBr + Na, RI + Na, the changes in activation energy would not be simply related to the changes in heat of reaction. In the reactions of sodium with hydrogen iodide and potassium with hydrogen bromide and iodide, the energy surfaces indicate clearly an increased probability of the collided state (*i.e.*, a small potential hollow in the configuration) and this explains the enhanced collision diameters (*loc. cit.*) which had to be introduced into the kinetic expression to account for the rates of these reactions. J. L. Magee [46] has recently calculated the energy surfaces for the sodium vapour–chlorine reactions and concluded that the reaction $Na_2 + Cl$ can occur by three possible mechanisms, two of which can lead directly to excited sodium atoms and the third to an excited sodium chloride molecule. He also calculates the absolute rates of the reactions by use of the transition-state method. Although all of these calculations are semi-empirical, the activation energies deduced are of the right order, and it may be justifiably concluded that the framework of the general scheme for the construction of potential-energy surfaces of the three-centre problem provides a reasonable picture and explains the characteristics of this wide group of reactions.

Luminescence and Quenching.—The potential-energy surfaces of the alkali–halogen reactions have also been useful in aiding the understanding of the chemiluminescence and quenching of the excited atoms. Evans and Polanyi [49] have shown that in the particular case of the reaction $Na_2 + Cl \longrightarrow Na + NaCl$, in which there is an absence of repulsion between the newly formed particles in the final electronic state of the activated complex, the reaction path shows that practically the whole of the energy is transformed into vibrations of the newly-formed molecule. Magee, on the other hand, by considering alternate mechanisms of the above reaction, concludes that a part of the luminescence may be produced by direct emission of radiation by the excited atoms produced in the reaction. Qualitative energy diagrams have also been employed by Ogg and Polanyi [45] to describe the primary chemiluminescence of the sodium–stannic chloride reaction (*loc. cit.*).

The observations of K. F. Bonhoeffer [50] and F. L. Mohler,[51] who reported a bright luminescence when hydrogen atoms were introduced into sodium

[48] A. G. Evans and M. G. Evans, *Trans. Faraday Soc.*, 1935, **31**, 1400.

[49] M. G. Evans and M. Polanyi, *ibid.*, 1939, **35**, 178; J. L. Magee, ref. (46).

[50] *Z. physikal. Chem.*, 1942, **113**, 199; 1925, **116**, 391.

[51] *Physical Rev.*, 1927, **29**, 419.

vapour at 200°, a slight luminescence with potassium, and none with rubidium and cæsium, have been discussed theoretically by J. L. Magee and Taikei Ri.[52] They show that the quenching reaction,

$$Na^* + 2H \longrightarrow Na + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is adiabatic, and by means of a model energy surface constructed by semi-empirical methods, they give a qualitative explanation of the experimental facts. The above authors consider that the quenching of excited sodium by hydrogen molecules is determined by the primary formation of an Na^*H_2 complex which undergoes an internal quenching and dissociation into $Na + H_2$. The theoretical evidence indicates that the Na^*H_2 state involves an attraction.

There is much other evidence to show that quenching of sodium fluorescence is not merely a direct exchange of energy by collision, but that chemical interaction between the excited atom and the gas-quenching particle takes place. V. Kondratjew and M. Siskin [53] have shown that the quenching efficiency of a number of molecules (O_2, N_2, CO, NO, I_2) is related in a general way to the strength of the bond which the atom in the molecule makes with sodium—a large quenching cross-section corresponds to an exothermic reaction of the type, $Na^* + AB \longrightarrow NaA + B$. Bawn and Evans [30] have observed with oxygen, nitric oxide, and hydrogen sulphide that effective quenching action corresponds to the direct chemical association, $Na^* + AB \longrightarrow NaAB^*$. Recently, K. J. Laidler [54] has treated the general question of quenching of excited sodium by the use of energy surfaces and concludes that the quenching by atoms is normally an inefficient process, but that with molecules the effect of the additional atoms is to stabilise a quenched complex which finally decomposes to give a deactivated atom and a vibrationally excited product. The pronounced ability of unsaturated hydrocarbons in quenching sodium resonance radiation has been qualitatively considered by R. G. W. Norrish and W. MacF. Smith [55] in terms of the crossing of energy surfaces. They conclude that the presence of unsaturation in the molecule manifests itself in a relatively large transmission probability for the transition between the surfaces.

C. E. H. B.

4. THE PHYSICAL CHEMISTRY OF LATENT-IMAGE FORMATION IN GELATINE–SILVER HALIDE EMULSIONS.

The formation of the photographic latent image has never been discussed coherently in these Reports, probably because its mode of formation was not fully understood and new theories were put forward at frequent intervals. Even now, ideas on detailed aspects are in a state of flux, but we are able to describe the formation of the latent image in terms of movements of electrons and ions in the silver halide (most commonly, silver bromide) crystals

[52] *J. Chem. Physics*, 1941, **9**, 638.

[53] *Physical. Z. Sowjetunion*, 1935, **8**, 644.

[54] *J. Chem. Physics*, 1942, **10**, 34.

[55] *Proc. Roy. Soc.*, 1940, *A*, **176**, 295.

containing a small amount of iodide which are the light-sensitive units in photographic emulsions. The mechanism of latent-image formation suggested by R. W. Gurney and N. F. Mott[1] may be said to have stood the test of time very much better than any previously advanced theory, and has proved to be valuable as a working hypothesis which has stimulated research considerably. It appears justifiable, therefore, to consider latent-image formation from their point of view, not attempting to discuss the merits or otherwise of all previous theories in detail.

The main puzzle we have to solve is this: Absorption of quite a few quanta of light by one of the small crystals or " grains " of silver halide in an emulsion renders this grain developable: treatment of the emulsion with a solution containing certain reducing agents will cause this grain to be reduced to metallic silver, whereas the unexposed grains are not so affected. We have to ask: (1) What is the change produced by the absorption of light? and (2) what is the mechanism of development and, in particular, how does a developer distinguish between exposed and unexposed grains?

There are many other subsidiary points to be considered as well, which are, however, all different aspects of the same two questions, and connected with differences in latent-image formation according to conditions of exposure, development, etc.

(1) *Nature of the Photographic Latent Image.*—When very large exposures are given to a photographic emulsion, the emulsion "prints out," *i.e.*, darkens visibly: the emulsion grains are reduced partly or wholly to metallic silver and bromine. This process is helped considerably if bromine acceptors are present. From these facts, early photographic workers deduced that the latent image itself is also a small speck of metallic silver[2] in more or less firm contact with the parent crystal. Other conceptions, *e.g.*, the sub-halide theory of the latent image,[3, 4] are now of mainly historical interest. Chemical investigation of latent-image silver is difficult because of the minute amounts involved, and also because the silver in its intimate contact with the silver halide behaves quite differently from free metallic silver. This finding seemed to support the sub-halide theory, until E. Baur[5] and W. Reinders[6] showed that " photo-halides " are adsorption complexes of silver and silver halide. The best indication of the nature of the latent image was obtained from the finding that on photolysis (*i.e.*, decomposition by exposure to light) of silver bromide, silver and bromine were the only products, and that the reaction curve of the bromination of silver has no kink,[7] thus excluding the possibility of formation of sub-halides. Crystal-structure investigations by *X*-rays of exposed silver halide layers showed that, apart from the silver halide, only silver was present.[8] In order to carry

[1] *Proc. Roy. Soc.*, 1938, *A*, **164**, 151.

[2] F. Guthrie, see note in (3).

[3] W. de W. Abney, " Instructions in Photography," London, 1882.

[4] M. Carey Lea, " Colloides Silber und die Photohaloide " (Ed. by H. Lüppo-Cramer, Dresden, 1918, Steinkopf).

[5] *Z. physikal. Chem.*, 1903, **45**, 613.

[6] *Ibid.*, 1911, **77**, 213, 356, 677.

[7] E. J. Hartung, *J.*, 1924, **125**, 2198.

[8] P. P. Koch and H. J. Vogler, *Ann. Physik*, 1925, **77**, 495.

out any of these investigations, much heavier exposures had to be applied than are necessary to produce the latent image. To assume that latent-image substance is metallic silver is therefore an extrapolation, although no argument has been advanced as to why this extrapolation should not be made.

By far the most sensitive detector of the latent image in an emulsion is still the process of development, but in that process the original latent image is lost. R. Hilsch and R. W. Pohl[9] have demonstrated a discoloration of large silver halide crystals by exposures to light of the order of that which would produce a latent image in photographic emulsions. They argue that this discoloration is not visible in photographic emulsions only because emulsion layers are so thin. Single crystals about 1 mm. thick were used, and the absorption of blue light by silver bromide crystals produced a new broad absorption band with a maximum at 6900 A. Absorption of light of wave-lengths falling into this band caused a bleaching around the wave-length used, leaving parts of the band unaffected.[10, 11] The band is thus not due to homogeneous particles, but to particles of a colloidal nature, the position of the absorption band depending upon the size of the particles. Absorption of light leads to destruction of the particles by a process to be discussed below. Here we note that red light can lead to a destruction also of the photographic latent image ("Herschel effect"). The wave-length sensitivity of the Herschel effect corresponds closely to the absorption band in discoloured silver halide crystals.[12, 13] All the experimental evidence available agrees with the conception that the result of exposing silver halides to light—and incidentally to certain other influences—is the production of small specks of colloidal silver, and the liberation of bromine.

(2) *Optical and Electrical Properties of Silver Halides.*—An understanding of the optical and electrical behaviour of silver halide crystals is essential for any consideration of the mechanism of latent-image formation. Most of the information recorded here was obtained from work on large single crystals, but is often applicable to the array of small crystals in a gelatine layer constituting an emulsion. The main difference lies in the larger surface area of the emulsion grains, which shows up in the spectral absorption.

(a) *Absorption of light.* Ionic crystals as a rule exhibit well-defined absorption bands. The silver halides constitute a notable exception to this rule. With these crystals, there is a " tail " on the long-wave-length side of the main absorption bands, which can be measured almost right across the visible spectrum.[14] The maximum of the main band corresponds to absorption of light in tightly bound ions in the body of the crystal; the long-wave-length tail is thought to be due to ions on surfaces, internal cracks and

[9] *Z. Physik*, 1930, **64**, 606.

[10] F. Löhle, *Nach. Ges. Wiss. Göttingen*, Math.-Phys. Kl, 1933, II, p. 271.

[11] J. H. de Boer, " Electron Emission and Absorption Phenomena," Cambridge, 1935, p. 299.

[12] B. H. Carroll and E. M. Kretchman, *J. Res. Nat. Bur. Stand.*, 1933, **10**, 449.

[13] O. Bartelt and H. Klug, *Z. Physik*, 1934, **89**, 779.

[14] J. Eggert and M. Biltz, *Trans. Faraday Soc.*, 1938, **34**, 892.

imperfections.[15] These ions must be more loosely bound than those in the body of the crystal. Their binding energy, and their spectral absorption, is affected considerably by any impurities that may be present.[16] Hence, the long-wave-length absorption of silver halides varies for different specimens according to their mode of preparation and is therefore often more characteristic for surface impurities present than for the body of the material. These effects are particularly pronounced for the silver halide emulsion grains because of their relatively large surface areas. Emulsions are usually prepared in a surplus of bromide ions, so that the grains are covered with bromine ions in excess of the stoicheiometric proportion. This causes a shift of the long-wave absorption limit towards longer wave-lengths; an even greater shift is obtained if the crystals are prepared in the presence of a surplus of silver ions.[17, 18, 19, 20]

The absorption of silver halides, and in many cases their photographic sensitivity, can be changed profoundly by the adsorption to the grain surfaces of sensitising dyes.[21] Photographic sensitivity can then be extended even into the infra-red. The adsorption process alters the absorption spectrum of the dyes, and it has been shown that the photographic sensitivity corresponds to that spectrum.[22] Dyes to act as efficient photographic sensitisers must fulfil certain conditions, such as planar structure, possibility of co-planar coupling of the electron transition in the silver halide and that in the dye, and tendency to aggregate formation. This was reported upon by R. A. Morton last year.[23]

The mechanism of latent-image formation, apart from the absorption of light, is identical in the dye-sensitised and the natural spectral sensitivity regions of silver halide grains. This is shown by the fact [24] that reciprocity failure curves * for different wave-lengths of light are parallel, if exposure is plotted against time of exposure; no doubt the curves would be identical if they were plotted in terms of number of quanta absorbed rather than of (visual) intensity. Latent-image distribution as between the surface and the interior of the grains was found to be identical, no matter whether light was absorbed in the natural or dye-sensitised sensitivity region.[25]

One dye molecule can be responsible for the production of as many as 50 atoms of silver,[26, 27] which means, as will be seen below, that that number of electrons is produced by one molecule. This is accounted for by assuming either (i) that an electron passes over from the dye to the crystal lattice and that the dye regains an electron by a mechanism as yet not understood, or (ii) that the dye molecule does not actually lose an electron, but passes its excitation energy on to the nearest bromine ion.[28] The energy deficits in both cases would have to be supplied by thermal energy, at the moment of electron transfer in case (ii), or afterwards in case (i). Supply of thermal energy seems essential for dye sensitisation to work. With many dyes, sensitisation breaks down at low temperatures, as would be expected,[29, 30] but this is not generally true.[31] This aspect of dye sensitisation requires further study.

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[15] See M. Ott, in Wien and Harms's "Handbuch der Experimentalphysik," XII, Part 1, Leipzig, 1932.

[16] K. F. Herzfeld, *Z. physikal. Chem.*, 1923, **105**, 329.

[17] W. Frankenburger, *ibid.*, p. 273.

[18] K. Fajans, *Z. Elektrochem.*, 1922, **28**, 499.

[19] W. Steiner, *Z. physikal. Chem.*, 1927, **125**, 275.

[20] K. Fajans and W. Steiner, *ibid.*, p. 307.

[21] H. Vogel, *Ber.*, 1873, **6**, 1302.

[22] J. A. Leermakers, B. H. Carroll, and C. J. Staud, *J. Chem. Physics*, 1937, **5**, 878; J. A. Leermakers, *ibid.*, p. 889.

[23] *Ann. Reports*, 1941, **38**, 7.

[24] J. H. Webb, *J. Opt. Soc. Amer.*, 1933, **23**, 318.

[25] W. F. Berg, A. Marriage, and G. W. W. Stevens, *Phot. J.*, 1941, **81**, 413.

* A reciprocity failure curve is a plot of the logarithm of the relative exposure (intensity × exposure time) required to produce a certain density on processing against the logarithm of either the intensity or the time of the exposure (see Fig. 3).

(b) *Electronic processes.* (i) Photo-conductivity. Absorption of light in the absorption tail of long wave-lengths produces an electronic conductivity in silver halide crystals.[32] These crystals are insulators at sufficiently low temperatures. The quantum equivalence of the production of electrons is of the order of 1 : for every quantum of light absorbed, one electron can be drawn across the crystal to the anode if the electric field strength is sufficient.[33] For smaller fields, the current across the crystal drops : some of the electrons are trapped at places where electrons can occupy empty states of lower energy. The nature of these traps is not known. The electrons carrying the current are considered to be liberated from the halide ions in the crystal and to pass over to a neighbouring silver ion, thus producing a halogen and a silver atom.[34] The electron is very loosely bound, and may be considered to be practically free to move about in the crystal from one silver atom to the next, its state of energy being referred to as " conduction level." Very small activation energies are involved in this movement, since photo-conductivity is not reduced until the temperature of the crystals is reduced to below 20° K.[35] The movement of the electrons in the conduction levels corresponds to thermal energy, the velocity being of the order of 10^7 cm./sec. Because of its high speed and frequent collisions with elements of the crystal structure, the electron gets near to any specified place in or on a silver halide grain within a very short space of time. This is the reason why the presence of even quite a small number of electron traps may be very effective in reducing photo-conductivity. Colloidal metal particles present in small numbers constitute very effective electron traps.[35] This means that the conduction levels of metallic silver are below those of the silver halide.[1]

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[26] W. Leszynski, *Z. wiss. Phot.*, 1926–27, **24,** 261.

[27] H. Tollert, *Z. physikal. Chem.*, 1929, *A*, **140,** 355.

[28] See S. E. Sheppard, *Atti* X *Cong. intern. Chim.*, 1938, **1,** 235.

[29] S. E. Sheppard, E. P. Wightman, and R. F. Quirk, *J. Physical Chem.*, 1934, **38,** 817.

[30] G. Ungar, *Z. Physik*, 1937, **106,** 322.

[31] J. H. Webb and G. H. Evans, *J. Opt. Soc. Amer.*, 1938, **28,** 249.

[32] Wilson, *Ann. Physik*, 1907, **22,** 107.

[33] W. Lehfeldt, *Nach. Ges. Wiss. Göttingen*, Math.-Phys. Kl, 1935, II, p. 170.

[34] K. Fajans and K. von Beckerath, *Z. physikal. Chem.*, 1921, **93,** 478.

[35] R. W. Pohl, *Proc. Roy. Soc.*, 1937, **49** (extra number), 1.

(ii) Halogen atoms. We have seen that absorption of light of suitable wave-length produces a silver and a halogen atom. Halogen is known to be set free during photolysis of silver halides,[7] and we must ask how it gets away from the crystal. If absorption of light occurs in a halogen ion on or near the surface, the halogen can be taken up by the moisture or gelatine surrounding an emulsion grain. If absorption occurs on an internal imperfection, the halogen atoms can move by a replacement process : an electron moving from a neighbouring halogen ion to the atom shifts the atom in effect to the place whence that electron came. Because of the " wave-mechanical tunnel effect " the activation energy for this process may be quite small, although there is no experimental evidence on this point.[36] The halogen atom may be trapped, however, by polarising the surrounding crystal structure and thus " digging its own hole " in the manner visualised by Mott.[37] For this process to occur, the atom has to remain stationary for about 10^{-8} sec. It has been suggested that high mobility of halogen atoms would make latent-image formation impossible, since they would follow the electrons and eventually rehalogenise any silver formed.[1] We must consider, however, that the halogen would proceed by diffusion; thus it has a very high chance of touching the surface of a grain before it reaches the latent-image silver speck. On reaching the surface, it would react with the surrounds of the grain immediately.

(c) *Ionic processes.* At normal temperatures, silver halide crystals are electrolytic conductors,[38] the current being carried exclusively by silver ions, which are smaller than the halogen ions.[39,40] The silver ions move by two different mechanisms, which appear to contribute approximately equal amounts to the observed conductivity.

(i) Interstitial ions. In thermal equilibrium, a certain number of silver ions occupy " interstitial " positions in the centre of the unit cube of the structure, which is distorted thereby. In these positions, the ions are mobile, requiring an activation energy of 8200 cals./mol. in silver bromide and 6500 cals./mol. in the chloride. The concentration of these interstitial ions is given by a formula of the type $C = C_0e^{-W/kT}$ and is always low at room temperature, of the order of 10^{-6} for silver bromide and 10^{-8} for the chloride, the energies of formation being 20,200 and 25,000 cals./mol. respectively. This means that, in an emulsion grain containing on the average 10^9 ion pairs, there are only 1000 interstitial ions for silver bromide and 10 for silver chloride. It is possible, however, that owing to impurities, the number of interstitial ions is higher than indicated by the formula; the curve of conductivity plotted against temperature shows a kink at about room temperature, indicating that the number of ions is higher than that corresponding to thermal equilibrium.[33, 39, 40, 41]

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[36] N. F. Mott and R. W. Gurney, " Electronic Processes in Ionic Crystals," Oxford, 1940.

[37] *Proc. Physical Soc.*, 1938, **50**, 186.

[38] See C. Tubandt, in Wien and Harms's " Handbuch der Experimentalphysik," VII, Part 2, Leipzig, 1928, p. 383 *et seq.*

[39] E. Koch and C. Wagner, *Z. physikal. Chem.*, 1937, *B*, **38**, 295.

[40] W. Jost, *Trans. Faraday Soc.*, 1938, **34**, 860.

(ii) Holes. The hole left in the structure when a silver ion moves into an interstitial position also has a certain mobility by a replacement mechanism : a neighbouring ion jumps into the hole, leaving a hole at the place whence it came. The activation energy for this process is approximately the same as that for the movement of interstitial ions.[39]

(3) *Latent-Image Formation.*—(a) *Mechanism.* How can the facts of photo-conductivity and ionic conductivity be used to account for the mechanism by which the silver atoms, formed by absorption of light all over the crystal, can collect in a small speck of metallic silver, situated on the surface of the grains where the developing solution can reach it ?

The clue to the answer was the discovery that photographic emulsions are relatively insensitive to light, unless certain impurities are present during emulsion making.[42, 43] These impurities were demonstrated to cause the production of silver sulphide specks on the grain surfaces [see Section 3, c]. The specks were regarded as nucleating centres on which the photolytically produced silver collects. The nucleating centres are now assumed to act by trapping the electrons liberated by light absorption. The centres thus become negatively charged and attract the mobile interstitial ions, which are discharged on the speck. In this way, a speck of metallic silver collects on the silver sulphide speck,[1] as is illustrated diagrammatically in Fig. 1.

The basic assumption, then, is that an electron in a silver sulphide speck can occupy states of lower energy than it can in the conduction levels of the silver halide. There is so far no experimental evidence supporting this assumption. Silver selenides and tellurides can also act as nucleating centres[44] and it is probable that other impurities, as well as mechanical imperfections, can similarly act as electron traps. These last two types of trap seem to come into action when the more efficient silver sulphide specks are overloaded or do not exist. This would seem to be clear from the fact that latent-image silver is also formed in the interior of photographic grains,[25, 46, 47, 48] where a normal developer does not reach and where silver sulphide specks do not seem,[25] and are in fact not likely, to occur.

(b) *Size of latent image.* It is commonly assumed that a silver speck has to be above a certain size to induce development, although its dimensions have never been determined directly for obvious reasons. Recourse was had to calculation, the amount of silver produced for heavy exposures being observed, and extrapolated down to the small exposures used to form a latent image. For photolysis, a quantum efficiency of the order of 1 has

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[41] W. F. Berg, *Proc. Roy. Soc.*, 1940, *A*, **174**, 559.

[42] T. Svedberg, *Phot. J.*, 1932, **62**, 310.

[43] S. E. Sheppard, *Coll. Symp. Monograph*, Wisconsin, 1923, p. 346.

[44] *Idem, Phot. J.*, 1925, **65**, 380.

[45] F. Kogelmann, " Isolierung der Substanz des latenten Bildes," Graz, 1894.

[46] H. Lüppo-Cramer, " Kolloidchemie and Photographie," 2nd Ed., Dresden, 1921.

[47] A. Kempf, *Z. wiss. Phot.*, 1937, **36**, 235.

[48] (Miss) G. Kornfeld, *J. Opt. Soc. Amer.*, 1941, **31**, 598.

been found by the classical investigations of Eggert and Noddack.[26, 49, 50, 51] Since statistical considerations of necessity come in, it is only possible to obtain certain upper and lower limits in this way. Other calculations are based on the shape of the toe of the characteristic curve,[52, 53, 54, 55, 56, 57] containing, in many cases, tacit and unwarranted assumptions on the mechanism of latent-image formation and growth. Sheppard [58] has given a comprehensive review of the question and concludes that in certain cases (at the threshold) * one, quite often a few, on the average (at a density of 1) a

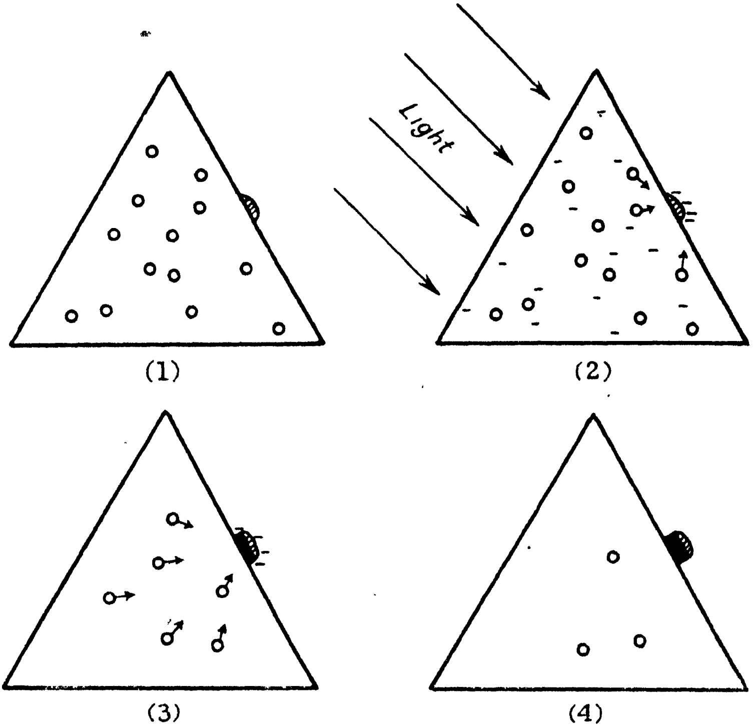

Fig. 1.

Latent image formation according to Gurney and Mott.

The triangles represent a silver halide grain. ○ = interstitial ions; — = electrons; shaded area = sensitivity speck; solid black area = latent image.

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[49] J. Eggert and W. Noddack, *Z. Physik*, 1923, **20**, 299.

[50] E. Mutter, *Z. wiss. Phot.*, 1928—29, **26**, 193.

[51] H. Kieser, *ibid.*, p. 1.

[52] T. Svedberg, *ibid.*, 1920—21, **20**, 36.

[53] T. Svedberg and H. Andersson, *Phot. J.*, 1921, **61**, 325.

[54] L. Silberstein and A. P. H. Trivelli, *J. Opt. Soc. Amer.*, 1938, **28**, 441.

[55] L. Silberstein, *ibid.*, 1941, **31**, 343.

[56] J. H. Webb, *ibid.*, p. 559.

[57] J. C. M. Brentano and S. Baxter, *Trans. Faraday Soc.*, 1940, **36**, 581.

[58] *Phot. J.*, 1931, **71**, 331.

See Fig. 2 for an explanation of technical terms.

few hundred, and sometimes several thousand quanta have to be absorbed by a grain. This does not mean that the size of the latent image varies within these limits. The most sensitive grains may already carry on their surfaces almost all the silver required before exposure : the very insensitive grains may be situated at the bottom of the emulsion layer, or the amount of silver formed may be distributed over several competing electron traps.[59, 60] Latent-image theory certainly has to account for the fact that certain grains can be made developable on formation of quite a few silver atoms. In contradiction to these conclusions, M. Savostjanova [61] claims that it is possible to " see " the colloidal silver particles produced by photolysis of silver halides under the ultra-microscope. This would require a diameter of the order of 1000 A. It has been suggested [62] that the particles are visible by a fluorescence process : electrons are lifted in energy from the silver to the silver halide conduction levels, and drop back emitting light. This suggestion has not been investigated experimentally.

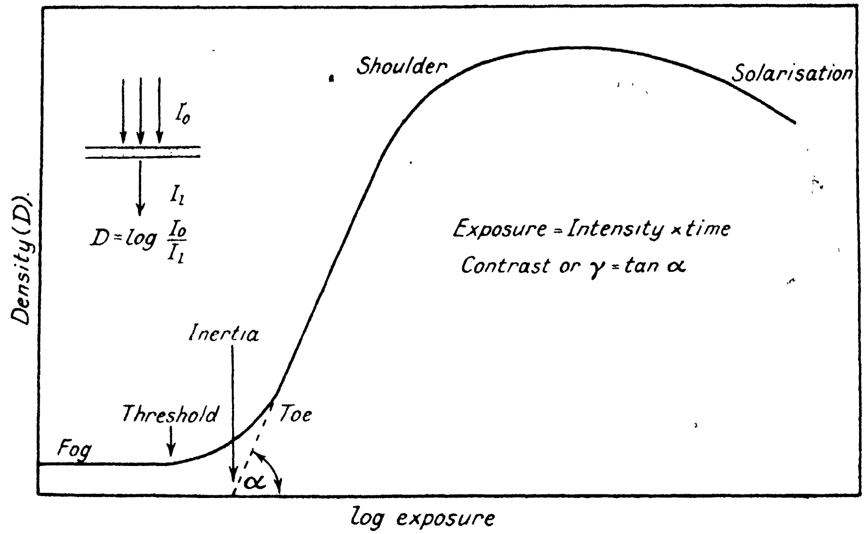

FIG. 2.

Diagrammatic characteristic curve of a photographic material, to explain technical terms.

(c) *Formation of sensitivity specks.* The recognition of the nature and investigation of the mode of formation of the sensitivity specks was one of the greatest experimental advances connected with latent-image research. It was found that most photographic gelatines contain sulphur compounds with groups S=C< which occur in *iso*thiocyanates and thiocarbamides

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[59] S. E. Sheppard, *Phot. J.*, 1928, **68**, 397.

[60] S. E. Sheppard, A. P. H. Trivelli, and R. P. Loveland, *J. Franklin Inst.*, 1925, **200**, 51.

[61] 9th Congrès International de Photographie, Paris, 1935, p. 94.

[62] W. F. Berg, *Trans. Faraday Soc.*, 1938, **34**, 889.

and can form addition complexes with silver halides. These complexes decompose on heat treatment, leaving specks of silver sulphide in intimate contact with the silver halide grains. Sheppard [44] and his collaborators were able to isolate the sensitising substances from the various by-products in gelatine manufacture. They followed up the various stages by testing for the presence of sensitisers by emulsion experiments, using photographically inert gelatines to which extracts of by-products were added. Sheppard and J. H. Hudson [63] investigated the formation of addition complexes. Sheppard [58] collected data on the amount of silver sulphide present in an emulsion of optimum sensitivity. An average figure is 5×10^{-4} g. of silver sulphide per g. of silver bromide.

Continued heating of an emulsion leads to an increase in the amount of silver sulphide and presumably in the size of the existing specks. Heat treatment, known as digestion, is an integral part of emulsion making and has to be controlled rigidly, since two disturbing photographic effects occur if digestion is over-done: the sensitivity of the emulsion drops, and the fog level rises, *i.e.*, grains are developable without exposure.[64] The drop in sensitivity is explained by the formation of several sensitivity specks on one grain competing with each other for the photolytic silver formed.[59] The increase in fog is accounted for by the production of oversize specks, which itself causes a drop in speed. The two effects are, however, distinct.[64]

(4) *Development.*—(a) *A few important data.* A grain is either developed completely or not at all. It is only with great difficulty that one can find partly developed grains [65, 66] by interrupting development at an early stage. Reduction of grains always begins at discrete points distributed over the surfaces of the grains.[52, 67] As soon as a grain becomes visibly reduced, reduction proceeds at a fairly high rate; different grains differ in the length of the induction period before visible reduction starts, according to their original sensitivity and the exposure they received. Large grains are on the whole more sensitive to light than small ones.[60]

The process of development shows many features of a reversible reaction, its kinetics following in a large measure the law of mass action; for instance, the rate of development is often proportional to the concentration of the developing substance.[65] Bromide ions in small amounts slow down the rate of development since they are a reaction product, thus reducing the rate of dissolution of silver bromide. (In large amounts, bromide ions exert a solvent action on silver bromide.)

Only in special cases, however, as, *e.g.*, with ferrous oxalate developers, is it permissible to regard development as a strictly reversible reaction. Side reactions usually occur.

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[63] *Z. wiss. Phot.*, 1927—28, **25**, 113.

[64] See, *e.g.*, B. H. Carroll and D. Hubbard, *J. Res. Nat. Bur. Stand.*, 1931, **7**, 219; 1933, **11**, 753.

[65] S. E. Sheppard and C. E. K. Mees, "Theory of the Photographic Process," London, 1907.

[66] T. Svedberg, *Phot. J.*, 1922, **62**, 186.

[67] M. B. Hodgson, *J. Franklin Inst.*, 1917, **184**, 705.

In thermodynamic equilibrium and therefore with a developer for which the reaction is reversible, the oxidation-reduction potential of the solution must lie between two well-defined limits. If the potential is too low, all silver halide grains, including the unexposed ones, will be reduced indiscriminately, if too high, the solution acts as an oxidiser, destroying the latent image.[65, 68] With developers as used in practice, however, the redox potential is often considerably below even that required to reduce unexposed silver bromide.

Not all reducing substances can serve as developing agents. Stannite ions are often quoted as being in all circumstances incapable of discriminating between exposed and unexposed grains.[69] Unprotected precipitates of silver halides are reduced by normal developers whether they are exposed or not; it is the presence of gelatine in conjunction with the electric double layer produced when precipitating silver halides in the presence of surplus bromide ions, which protects unexposed grains from reduction.[69]

Silver ions in solutions are adsorbed to metallic silver.[69]

The rate of development is influenced strongly by the surface conditions of the grains, say, by adsorption of certain dyes.[69]

The curve of density against time of development goes straight through the origin, and has its greatest slope at the origin for developers with neutral molecules, like *p*-phenylenediamine and related compounds.[70] For ionised developer molecules, the density–time curve has a region of zero slope near the origin, followed by a region of increasing slope (a " toe ").

The developed silver was shown by photomicrographs [71] and the electron microscope [72] to be in the form of a tangled mass of thin threads or filaments.

(b) *Supersaturation theory of development.* For a long time the supersaturation theory of development, due to R. Abegg [73, 74] and W. Ostwald,[75] was held to be valid. The silver halide is supposed to dissolve in the developing solution, the silver ions being reduced to atoms which then precipitate on the latent image speck which acts as a nucleus. Many objections have been advanced against this theory and it is now mainly of historical interest. The solubility of silver halides is much too low to account for rates of development as normally obtained, and unexposed grains are not dissolved.[76]

(c) *Development : a heterogeneous catalysed reaction.* M. Volmer [76] first indicated the view, now widely held, that the distinction between exposed and unexposed grains is due to a different rate of development. The reaction is catalysed by the latent image and each grain is reduced as an entity. This conception has been most successful in accounting for the facts

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[68] W. Reinders, *J. Physical Chem.*, 1934, **38**, 784.

[69] T. H. James and G. Kornfeld, *Chem. Reviews*, 1942, **30**, 1.

[70] T. H. James, *J. Physical Chem.*, 1939, **43**, 701.

[71] F. E. C. Scheffer, *Brit. J. Phot.*, 1907, **54**, 116, 271.

[72] C. E. Hall and A. L. Schoen, *J. Opt. Soc. Amer.*, 1941, **31**, 281.

[73] *Ann. Physik*, 1897, **67**, 425.

[74] *Arch. wiss. Phot.*, 1899, **1**, 15.

[75] " Lehrb. der Allg. Chemie," Leipzig, 1893, Vol. 2, part I.

[76] *Z. wiss. Phot.*, 1920—21, **20**, 189.

of development, but the way the catalysis works is still under discussion. Gurney and Mott[1] suggested that development functions by a mechanism analogous to latent-image formation, electrons being handed over from the developer into the latent-image speck. Interstitial silver ions then move up from the interior of the crystal and deposit on the latent image. This provides a beautiful account of the threadlike shape of the developed silver, but serious objections have been raised,[69] one of them being that the mechanism does not provide for the escape of halide ions from the grain. The mechanism is not complete, since it does not account for the influence of the surface conditions of the grains on the rate of development. T. H. James and (Miss) G. Kornfeld[69] consider that the reaction takes place on the triple interface of latent-image silver, silver halide crystal, and solution. Some of the silver ions of the crystal are considered to be " adsorbed " to the latent image, which thus reduces the activation energy required for a developing molecule to reduce a silver ion. The rate of development depends on the rate at which developer molecules can reach the adsorption site and on the number of silver ions there. This accounts for the effect of surface layers on the rate of development, both mechanical and electrical influences interfering with the approach of developer molecules. The reaction would tend to proceed chiefly along surfaces and cracks and thus produce silver in filamentary form, an explanation which is, perhaps, the weakest point on an otherwise very satisfactory picture.

(5) *Photographic Effects.*—The theoretical picture of latent-image formation given above enables us to account for many of the more detailed features of the photographic process. On the other hand, we record here data which made it possible for several photographic effects to be accounted for in terms of each other; these data are of value regardless of any theories.

The effects discussed now, and some others, are summarised in the chart on pp. 66, 67.

The recognition that both electronic and ionic processes are involved in latent-image formation gave a clue to the explanation of the effects known as reciprocity failure. The two processes have different time constants and temperature coefficients; this makes it clear why optimum sensitivity is often found at a certain intensity level. Under certain conditions of exposure, the processes can be separated in time and to some extent studied separately.

(a) *Reciprocity failure.* The photochemical reciprocity law which holds for single-stage reactions states that the same product $I \times t$ of intensity of light I and time of exposure t will produce the same effect, regardless of the values of I and t.[77] For the double-stage photographic reaction this law cannot be expected to hold : with most materials there is an optimum sensitivity at a certain exposure time and intensity, and sensitivity falls off at both higher and lower intensities, so that we speak of high- or low-intensity reciprocity failure (see Fig. 3).

[77] R. Bunsen and H. E. Roscoe, *Ann. Physik,* 1855, **96**, 373; 1857, **100**, 43, 481; 1858, **101**, 235; 1859, **108**, 193; 1862, **117**, 529.

(i) *Low-intensity reciprocity failure.* C. E. Weinland [78] and J. H. Webb and C. H. Evans [79] have demonstrated that low-intensity reciprocity failure is due to inefficiencies of latent-image formation in its first stages of growth. Stable, but not yet developable silver specks can be produced much more efficiently at shorter times of exposure and thus at higher intensities. A low-intensity exposure following one at high intensity is as efficient as the latter if it comprises approximately half the total exposure required. Two reasons for the inefficiency of a low-intensity exposure have been advanced. The latent-image speck may not be able to grow unless a certain minimum concentration of electrons is reached in a grain.[1] At low intensities this will never be reached because electrons are lost all the time by recombination. Webb and Evans [79] assume that a speck of silver actually begins to form but disintegrates by thermal agitation into electrons and interstitial silver ions. At the moment, a decision between these very similar mechanisms is not possible; a process using up electrons in some other way is necessary to account for low-intensity failure, but this has not been studied or understood.

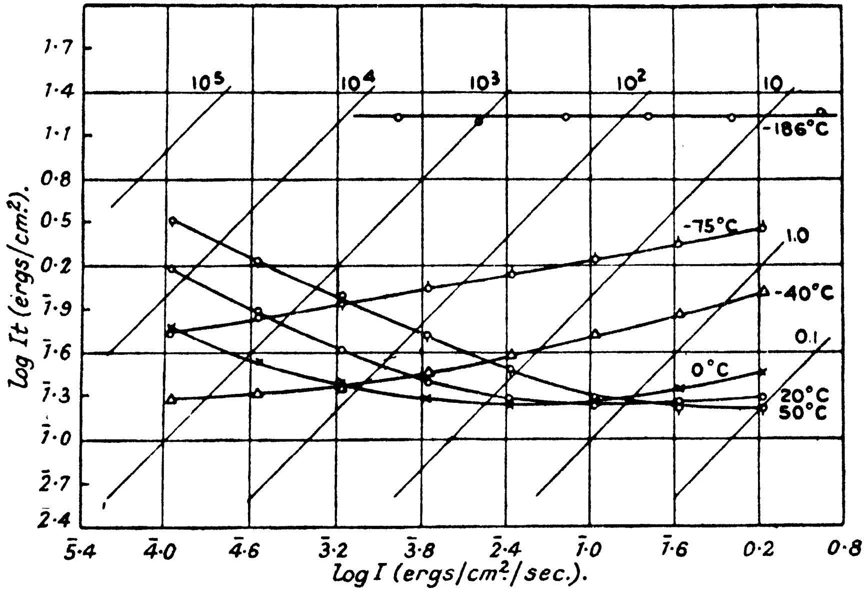

Fig. 3.

Reciprocity failure of a photographic material at different temperatures. The log *It* necessary to produce a constant density is plotted against log *I* [Fig. 77 of Mees's book (see p. 68)].

(ii) *Hypersensitisation and latent-image intensification.* Weinland's [78] and Webb and Evans's [79] results demonstrated that low-intensity failure can be largely eliminated by giving a uniform pre-exposure at higher intensities, thus hypersensitising the photographic material. The reverse process is also practised and is known as latent-image intensification or "latensification";[80, 81] an under-exposed picture obtained at a high intensity of light can be intensified by a uniform post-exposure of long duration and low intensity. These two effects are thus simply a manifestation of the existence of low-intensity reciprocity failure.

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[78] *J. Opt. Soc. Amer.*, 1927, **15**, 337; 1928, **16**, 295. [79] *Phot. J.*, 1940, **80**, 188.

(iii) *High-intensity reciprocity failure.* High-intensity reciprocity failure seems to be fairly well understood. At high intensities the ionic process is not sufficiently fast to neutralise the electrons colliding with the sensitivity specks, which become charged to capacity and repel any further electrons.[1] As a consequence, latent image is formed elsewhere in and on the grain,[25, 82] presumably on electron traps which for normal intensities would not be effective in holding electrons long enough for a latent image to be formed, or on places where a high momentary electron concentration causes the lattice to break down so as to form a silver speck. More latent image is formed in the interior of the grains, the higher the intensity of light; [25] this means that high-intensity reciprocity failure occurs only with latent image situated at the surface of the grains, and will therefore vary according to the amount of silver halide solvent in the developer and the duration of development.[25, 83] High-intensity reciprocity failure is thus characterised by a change in distribution of the latent image; there is no evidence to suggest that the total amount of silver formed decreases with increasing intensity.

(iv) *Very high intensities.* At very high intensities, a state is reached where, as far as the ionic process is concerned, electrons are released practically instantaneously: shortening the exposure time still further does not result in a further change in the mode of latent-image formation, and reciprocity failure is absent.[41] At an exposure time of about 4×10^{-5} sec. the reciprocity failure curve (see footnote, p. 52, and Fig. 3) of 4 materials tested bent over into the horizontal. The bend-over point shifts towards long times of exposure with decreasing temperature, depending on the mobility of the ions, which varies with temperature as $e^{-E/kT}$. This is because, below room temperatures, the number of interstitial ions is constant,[33] the conductivity varying as the mobility. In contradiction to this, Webb [84] has found from an investigation of the influence of temperature on reciprocity failure, that the concentration of interstitial ions varies down to very low temperatures; this contradiction has not been cleared up.

(v) *Effect of temperature on photographic sensitivity.* Webb [85] has cleared up a controversy of long standing by demonstrating that the temperature coefficient of photographic sensitivity depends largely on the intensity level of the exposure. The change in reciprocity failure characteristics with temperature as shown in Fig. 3 can be accounted for, at least qualitatively,

[80] G. E. Moore, *Phot. J.*, 1941, **81**, 27.

[81] *Amer. Cinematogr.*, 1940, **21**, 499; *Kinematograph Weekly*, 1941, **295**, 15.

[82] *Phot. Corr.*, 1936, **72**, 1.

[83] L. W. Strock, *Norske Vidensk. Skr.*, 1938, I, Mat.-Naturv. Klasse, No. 10.

[84] *J. Opt. Soc. Amer.*, 1942, **32**, 299.

[85] *Ibid.*, 1935, **25**, 4.

on the basis of the mechanism described. The drop in ionic mobility at reduced temperature affects the branch of the reciprocity failure curve on the high-intensity side of the optimum: at low temperatures, repulsion of electrons from a sensitivity speck occurs at an intensity where at normal temperatures the mobility of the ions is quite sufficient to discharge some of the electrons on the speck during the exposure. Thus the whole high-intensity branch shifts towards lower intensities at reduced, and towards higher intensities at elevated temperatures.

Low-intensity failure is affected in a similar fashion, but for a different reason. Here, the stability of a small speck of silver depends on temperature, the probability of an electron being lost from the speck in a time interval depending on temperature as $e^{-W/kT}$. The temperature coefficient for the processes responsible for high- and low-intensity failure being different, the shape of the reciprocity failure curve alters somewhat with temperature; the most important effect, however, is a bodily shift of the whole curve towards lower intensities as the temperature is decreased.

(vi) *Intermittency effect.* An intermittent exposure sometimes gives higher, sometimes lower density than an uninterrupted equal exposure at the intensity of the flashes. Webb [86] has shown up the long suspected [65] connection between this effect and reciprocity failure. At a sufficiently high rate of interruption, a state is achieved when on the average a single quantum of light is received by each grain for each flash of light passed by a rotating sector. For higher speeds of rotation of the sector, the incidence of quanta on any one grain is not altered and corresponds to the average light intensity passed by the sector. On varying the speed of the sector from standstill to high speed, at the ends of this range we are dealing with exposures at two well-defined intensities at which, according to the reciprocity characteristics of the material, photographic sensitivity is different. According to whether the intensities fall on the high- or the low-intensity branch of the reciprocity failure curve, the continuous or the interrupted exposure will produce a higher density. A sector operating at very high speeds is thus a convenient means of providing a scale of intensities for photometric use.

(vii) *Very low temperatures.* At sufficiently low temperatures, the flat, high-intensity branch of the reciprocity curve [41] occupies the whole range of intensities and exposure times practicable: reciprocity failure disappears entirely.[87, 88] Here we have a complete separation of at least the first part of the electronic from the ionic process. In order to account for the fact that photographic sensitivity persists at very low temperatures, it is necessary to assume that electrons are trapped in the grains so as to prevent them from recombining; on warming, the ionic process occurs. It has been demonstrated that the latent image is in a fairly labile state until the material is warmed: red light frees the electrons very effectively from their traps, so that a latent density is easily bleached out; after the warming, this is no longer possible.[31, 89] The electron traps are of two kinds: the sensitivity specks, which are of the order of one volt deep and hold the electrons tightly, and shallower, less well specifiable traps, from which electrons are released on warming. The small capacity of the sensitivity specks enables only the most sensitive ones to take up a sufficiently large number of electrons during a single low-temperature exposure; hence the loss in sensitivity. Repeated exposures with intervening periods of warming increase the sensitivity to a value approaching that of room temperature.[31] The loss in sensitivity affects in the main the surface latent image, which is formed by the help of silver sulphide specks. The internal image sensitivity is but slightly affected, demonstrating that its mode of formation is different from that of the surface image.[25] Changes in latent-image distribution thus do not account for the drop in practical speed at low temperatures. A drop in speed and contrast occurs even between 90° and 20° K.,[87] although at the higher temperature ionic conductivity is already zero. At 4° K. photographic sensitivity still persists.[89] The changes occurring at these very low temperatures are not understood.

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[86] *J. Opt. Soc. Amer.*, 1933, **23**, 157.

[87] W. F. Berg and K. Mendelssohn, *Proc. Roy. Soc.*, 1938, *A*, **168**, 168.

[88] C. H. Evans and E. Hirschlaff, *J. Opt. Soc. Amer.*, 1939, **29**, 164.

(b) *Herschel effect.* The Herschel effect is the bleaching out of a latent density (originally of a print-out density) by red or infra-red light. In general terms, it is accounted for by a reversal of latent-image formation: light can eject electrons from the silver speck, the electrons are trapped outside the latent image, and silver ions leave the speck, going back into the silver halide lattice as interstitial ions.[1] All experimental evidence agrees with this conception, except that we cannot account for the method of electron trapping. It has been suggested that the Herschel effect consists in a dispersal of the latent image, the total amount of silver present not being affected: this has not been proved convincingly.[27, 90, 91] The effect is stronger the higher the intensity of the first exposure: the numerous small specks of latent-image silver obtained at high intensities are more readily destroyed than the larger ones produced by a low intensity exposure.

(c) *Clayden effect.* In the following series of influences, *viz.*, pressure, *X*-rays, very brief exposure to light, normal exposure to light, any of the preceding ones desensitises a photographic material towards a subsequent one if given as a pre-exposure.[92] The combination of a brief followed by a normal exposure to light has been investigated more fully than the others, and the results are presumably valid for the whole series. As suggested by Lüppo-Cramer,[82] the brief exposure produces internal latent-image specks, which compete with those on the surface for the latent image formed by the subsequent exposure of normal duration.[25] A similar effect occurs when a low-temperature exposure is followed by one at room temperature;[89] we do not know where this fits into the series of influences quoted.

(d) *Solarisation.* Solarisation is the phenomenon in which, with certain photographic materials, continued increase in exposure eventually leads to a drop in developed density. This only occurs with the surface latent image [25] and can be removed by treating the emulsion with a halogen acceptor before exposure [3] or a silver halide solvent afterwards.[93] The effect is caused by the bromine atoms which are formed by the exposure; they leave the grains, attack the surface image, and form a coating of silver halide through which a normal developer cannot act. Solarisation can be removed to some extent by prolonged development [25] because of the slight solvent action of the constituents of a normal developer.

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[89] W. F. Berg, *Trans. Faraday Soc.*, 1939, **35**, 445.

[90] W. Leszynski, *Z. wiss. Phot.*, 1926—27, **24**, 275.

[91] A. P. H. Trivelli, *J. Franklin Inst.*, 1929, **207**, 765.

[92] R. W. Wood, *Phil. Mag.*, 1903, **6**, 577.

(e) *Albert reversal.* Another effect connected with latent-image distribution and the formation of internal latent image is the Albert reversal,[94] which is the finding that, if a material is treated with chromic acid after a preliminary exposure, a subsequent exposure will form a positive. The effect was at first accounted for by assuming that a combination of sensitivity speck and latent image was destroyed the more readily the larger the latent-image specks, so that the grains became desensitised more the larger the first exposure had been.[95] G. W. W. Stevens [96] has shown that the desensitisation is due to internal latent-image nuclei produced by the first exposure. This accounts for the finding that the effect is largest for very brief first exposures, and that it does not occur if physical development after fixation is used.

(f) *Sabatier reversal.* A photographic material, if pre-exposed and developed for a short time, gives a positive image with a second exposure. Optical screening by the density of the image developed after the first exposure is to a large measure responsible for the reversal,[97] but it has also been shown that a desensitisation of grains occurs during the first development,[98] since chemical " fogging agents " like sodium arsenite can produce reversal. The mechanism of this desensitisation is not clear. It has been suggested that silver is transferred from developing to neighbouring grains which are thereby desensitised. Silver transfer has, in fact, been demonstrated,[98] but why this should have a desensitising rather than a sensitising action is difficult to see, unless the silver is deposited in a very disperse state. The specks would have to be too small to act as latent-image specks, but large enough to compete with each other and any sensitivity specks present for any latent-image silver subsequently formed.[98]

(g) *High-energy quanta.* Many of the effects discussed so far are due to the fact that a single quantum of light representing a small amount of radiating energy is unable to make a grain developable. In many respects the photographic process is simplified when high-energy quanta, as of *X*-rays, or particles, as α-rays, protons, or high-speed electrons, are used. With these, as a rule, no more than one quantum or particle is required to make a

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[93] J. E. Nafe and G. E. M. Jauncey, *Physical Rev.*, 1940, **57**, 1048.

[94] Albert, *Arch. wiss. Phot.*, 1899, **1**, 285.

[95] W. Clark, *Phot. J.*, 1923, **63**, 30; 1924, **64**, 91.

[96] *Ibid.*, 1939, **79**, 21.

[97] A. Marriage, *ibid.*, 1937, **77**, 619.

[98] G. W. W. Stevens and R. G. W. Norrish, *ibid.*, 1938, **78**, 513.

Photographic Effects.

Effect.	1st Exposure.		Intermediate treatment.	2nd Exposure.		Remarks.	
	I.	*t.*		*I.*	*t.*		
Reciprocity failure: low intensities (5, a, i)	low ←	long →	—	—	—	D = const.	speed decreases ←
high intensities (5, a, iii)	high →	short ←	—	—	—	D = const.	speed decreases ←
	v. high →	v. short ←	—	—	—		speed constant
Hypersensitisation by pre-exposure (5, a, ii)	high	short	—	low ←	long →	1st uniform 2nd camera	speed of 2nd exposure increases →
Latent-image intensification (5, a, ii)	high	short	—	low ←	long →	1st camera 2nd uniform	speed of 1st exposure increases →
Temperature: reduced (5, a, v)	low ←	long →	—	—	—	—	speed increases →
	high →	short ←	—	—	—	—	speed decreases ←
very low (5, a, vii)	Independent of intensity			—	—	—	speed always lower than optimum at room temp.
increased (5, a, v)	low ←	long →	—	—	—	—	speed decreases ←
	high →	short ←	—	—	—	—	speed increases →
Intermittent exposures (5, a, vi) Schwarzschild effect	high →	short ←	—	—	—	(often)	speed increases →
	low ←	long →	—	—	—	—	speed decreases ←
high frequency	—	—	—	—	—	Result according to average intensity	
Solarisation (5, d)	Continued exposure			—	—	Only for surface image	Reversal
Herschel:				—			Bleaching or reversal of:
visual (5, b)	White light		—	Red light		—	print-out density
latent (5, b)	,,		—	,,		—	latent density
low temp. (5, a, vii)	At very low temp.		Keep cold	,,		—	very effective bleaching
			Warm up	,,		—	no bleaching
Dye reversal [102, 105]	White light		Dyeing	Light absorbed by dye		Only with certain dyes	Reversal
Seebeck [103]	White light		—	Coloured light		—	Print-out image in colour of second exposure

Becquerel [103, 106]	White light	—	Yellow or red	AgI emulsions physical dev. chemical dev.	Print-out positive image of second exposure Developed positive image of second exposure Herschel reversal
Weigert [104, 105, 107]	Uniform, white polarised Polarised	— —	Polarised, coloured —	According to wave-length —	Dichroic print-out images Dichroic developed density
Clayden (5, c)	v. high v. short	—	Normal or low Normal or long	Surface latent image Internal latent image	Desensitisation towards 2nd exposure Sensitisation towards 2nd exposure
Very low temp. (5, a, vii)	At very low temp. to light	Warm up	Exposure to light	—	Desensitisation towards 2nd exposure
Villard [105] **(5, c)**	X-Rays	—	Light	—	Desensitisation towards 2nd exposure
Pressure (5, c)	Pressure ,,	— —	Light —	—	Desensitisation towards 2nd exposure Produces some latent image
Russel [105]	Contact with metal and other substances ,, ,,	— —	— Light	— (often)	Produces latent image Desensitisation towards 2nd exposure
Sterry [105, 108]	Light	Chromates	—	—	Lowering of contrast
Albert (5, e)	Uniform to light	Chromic acid	Stepped to light	Surface image Internal image	Reversed speed increases
Sabatier (5, f)	Uniform to light	Partly developed	Stopped to light or Na_2HAsO_4	—	Reversal of 2nd exposure
Purkinje	Difference in contrast for light of different wave-lengths				
Kron [105]	Shift of optimum of reciprocity failure curve towards high intensities with increasing time of development.				
Ross [105]	Contraction of small images due to tanning action of developer				
Lainer [105]	Speed increase by treatment with iodide, revealing internal image (Keimblosslegung)				
Capri-blue [105, 109]	Increase in speed and contrast of coarse-grain emulsions without silver sulphide sensitivity specks by certain dyes				
Eberhard and Kostinsky [105, 110]	Value of a developed density depends on neighbouring density: produced by developer reaction products				
High-energy quanta or particles, as X-rays, X-ray protons, fast electrons, show : (5, g)	(1) Straight line density–time characteristics, highest slope at origin (2) Same shape characteristics for all wave-lengths (3) Absence of reciprocity failure				

Note.—Underline arrows are used to indicate the direction of an effect. For instance, with low-intensity failure the $\underleftarrow{\text{speed}}$ decreases with decreasing $\underleftarrow{I}$ and increasing $\underrightarrow{t}$. References are either to sections in the Report or to papers in the bibliography.

grain developable; certain fast particles will even cause a string of grains to be made developable. Exposures to X-rays have been studied very extensively, and, in confirmation of our conceptions on latent-image formation, it is found that there is no reciprocity failure,[99] that therefore time- and intensity-scale curves can be used interchangeably, and that the characteristic curves are of identical shape for all wave-lengths if referred to the number of quanta absorbed.[100] A density–exposure time or intensity curve is straight at the origin through which it passes. Solarisation is found with X-rays.[101]

(6) *Outstanding Questions.*—On the whole, the theory of the photographic process is reasonably coherent, but attention may be directed to a few features not sufficiently understood. Some of these difficulties have already been mentioned in the body of the Report. What are the basic reasons for the big differences in photographic sensitivity between silver bromide, chloride, and iodide emulsions? What are the reasons which so far have enabled gelatine emulsions to be made much more sensitive than those in any other binding medium? What is the mechanism of desensitisation by certain dyes, and of the reversal obtained, if an exposed material is desensitised by a dye and exposed still further? [11, 102, 103] What is the explanation of the Weigert effects,[104] the finding that polarised red light is capable of making a print-out density dichroic with certain emulsions, and that a latent image produced by polarised light leads to a dichroic image on processing? The mechanism of development still requires a great deal of attention. Future work will be followed with interest, not only by photographic technicians but by anybody concerned with the questions of catalysis and heterogeneous reactions, reactions involving solids, and photochemistry.

As reviews should be noted:

W. Meidinger, in Hay's "Handbuch der Photographie," Vol. V, Springer, Wien, 1932. (Very full bibliography up to early 1932.)

C. E. K. Mees, "The Theory of the Photographic Process," Macmillan, New York, 1942. (Very comprehensive review.)

N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Oxford, Clarendon Press, 1940. (For a discussion of the fundamental processes.)

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[99] W. Friedrich and P. P. Koch, *Ann. Physik*, 1914, **45**, 399.

[100] R. Glocker and W. Traub, *Physikal. Z.*, 1921, **22**, 345.

[101] K. Schaum, *Arch. wiss. Phot.*, 1904, **18**, 77.

[102] J. Waterhouse, *Proc. Roy. Soc.*, 1875, **29**, 186.

[103] H. Lüppo-Cramer, Eder's "Handbuch der Photographie," Vol. 2, Part I (1923), Vol. 3, Part III (1933), Wien.

[104] See H. Freundlich, *Phot. J.*, 1936, **76**, 395.

[105] *Phototechnique*, Feb., 1940, p. 48.

[106] H. Lüppo-Cramer, *Phot. Korr.*, 1939, **75**, 49.

[107] F. Weigert and J. Matulis, *Koll-chem. Beihefte*, 1933, **38**, 384.

[108] J. Sterry, *Phot. J.*, 1904, **44**, 50.

[109] H. Lüppo-Cramer, *Phot. Ind.*, 1940, **38**, 271.

[110] F. E. Ross, "The Physics of the developed Photographic Image," D. van Nostrand, 1924, New York.

S. E. Sheppard and C. E. K. Mees, "Investigations on the Theory of the Photographic Process," Longmans & Co., London, 1907. (For the basic studies on development.)

W. F. Berg, "Latent Image Formation," *Trans. Faraday Soc.* (in the press).

W. F. B.

C. E. H. Bawn.
W. F. Berg.
G. Gee.
H. W. Melville.

INORGANIC CHEMISTRY.

1. GENERAL.

THE first section of this Report deals with a wide range of publications which have appeared or become available during the past year. Topics for inclusion have been selected on the basis of their general interest rather than of their value to the specialist: the arrangement follows the order of the groups of the Periodic Table. The second and the third section of the Report are devoted to the Luminescence of Inorganic Solids and the Technique of Inorganic Chemistry, respectively. In discussing the first of these topics it has been necessary to deal in an elementary manner with the underlying physical principles, but as far as possible emphasis has been placed on those aspects of the subject which are of interest in inorganic chemistry. The final section, dealing with technique, needs little introduction. The development of new technique or, more commonly, the application of physical and physico-chemical technique, has time and again paved the way for new and important developments. The summary given here, though far from complete, may, it is hoped, serve to stimulate further interest in the experimental study of Inorganic Chemistry.

Since the preparation of the last *Annual Report* there has been a sustained interest in the separation or enrichment of isotopes, and in applications of enriched material in "tracer" experiments. Application of the thermal diffusion method to the treatment of methane, for example, has given yields up to 0·3 g./48 hr. of methane in which the ^{13}C : ^{12}C isotope ratio is increased to 11·5 times the normal value.[1] The neon isotopes have been obtained in a pure state by the same method.[2] In this work a separation tube 29 m. long was used. The isotopes ^{20}Ne and ^{22}Ne were obtained in quantity with a purity of 99·7—99·8%, and a fraction was isolated in which the concentration of the rare isotope ^{21}Ne was enriched from the normal value of 0·27% to 2·5%. The same technique has been applied for separating from normal krypton a mixture containing 22% of ^{84}Kr and 78% of ^{86}Kr.[3]

The efficiency of the electrolytic separation of the chlorine isotopes at a platinum anode has been investigated.[4] The electrolytic separation factor for these isotopes in the range 25—40° was found to be 1·0060 $\pm$ 0·0005, a value which is about the same as that on Acheson graphite. The separation factor for chlorine is about the same as that for the oxygen isotopes and is considerably less than that for the hydrogen isotopes. An interesting feature of this work was the use of measurements of the temperature of flotation in ethylene dibromide of annealed sodium chloride crystals as a means of determining the isotopic composition of samples. Radioactive isotopes of chlorine and bromine have been used as tracers in studying the exchange in carbon tetrachloride solution between the free halogens and the phosphorus tri- and penta-halides. In each case exchange was complete in less than 3 minutes, and the experiments were taken as an indication of the equivalence of the halogen atoms in the phosphorus halides.[5]

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[1] A. O. Nier and J. Bardeen, *J. Chem. Physics*, 1941, **9**, 690.

[2] G. Diekel and K. Clusius, *Z. physikal. Chem.*, 1940, *B*, **48**, 50.

[3] *Idem*, *Naturwiss.*, 1940, **28**, 711.

[4] H. L. Johnston and D. A. Hutchison, *J. Chem. Physics*, 1942, **10**, 469.

The exchange of radioactive silver in solution with silver ions in silver chloride suspensions has been shown to occur.[6] It is not confined to the crystal surface, but is propagated into its bulk, probably by a process of self-diffusion. It was found that adsorption of fluorescein, eosin, methylene-blue, or wood violet on the silver halide grains had very little, if any, influence on the rate of attainment of equilibrium. The exchange was reversible in the sense that, when the precipitate contained the radioactive silver initially and the solution was inactive, the activity of the solution increased up to a value corresponding with a homogeneous distribution of the radioactive silver.

Sodium monothio-orthophosphate, Na_3PO_3S, has been prepared by heating together at 450—750° in a vacuum or an inert atmosphere the calculated quantities of sodium metaphosphate and sodium sulphide.[7] The product was 70—87% pure, depending on the reaction temperature, but the pure hydrated compound $Na_3PO_3S,12H_2O$, was readily isolated by re-crystallisation from warm water. This method of preparation is more convenient than those depending on the decomposition of thiophosphoryl chloride with alkali or the fractional hydrolysis of phosphorus pentasulphide with alkali. The compound, like trisodium orthophosphate, exists in two modifications, the transition temperature being approximately 550°. The same authors have also shown [8] that when sodium phosphate is heated at temperatures up to 1100° with silica or sodium silicate, there is no evidence that the sodium silicophosphate, $Na_8[Si(PO_4)_4]$, described by R. Schwarz,[9] is formed.

A lower oxide of boron with the empirical formula BO is formed when elementary boron is heated with zirconium dioxide in a vacuum at 1800°.[10] The reactants were heated together in a tantalum boat in a high-frequency furnace. The boron oxide was volatile at the reaction temperature, and condensed as a light brown, amorphous solid, which was obtained in sufficient quantities for analysis. The compound obtained by this thermal reduction method is almost certainly different from the oxide B_2O_2 obtained by R. C. Ray and P. C. Sinha [11] from the product of hydrolysis of magnesium boride. Repeated extraction of magnesium boride with water yields a residue which reacts with aqueous ammonia forming two salts, $(NH_4)_2B_2(OH)_2$ and $(NH_4)_2B_4O_6$, which were separated by fractional crystallisation. These two salts when heated lost, in the first case, ammonia and hydrogen in equal volumes, and in the second, ammonia : the solid residues had the compositions B_2O_2 and B_4O_5, respectively. Both of these oxides were soluble in water and their solutions had reducing properties.

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[5] W. Koskoski and R. D. Fowler, *J. Amer. Chem. Soc.*, 1942, **64,** 850.

[6] A. Langer, *J. Chem. Physics*, 1942, **10,** 321.

[7] E. Zintl and W. Morawietz, *Z. anorg. Chem.*, 1940, **245,** 16.

[8] *Ibid.*, p. 12.

[9] *Ibid.*, 1928, **176,** 236.

[10] E. Zintl, W. Morawietz, and E. Gastinger, *ibid.*, 1940, **245,** 8.

[11] *J.*, 1941, 742.

A volatile gallium hydride, Ga_2H_6, has now been described.[12] The first stage in the preparation of this important compound is the synthesis of tetramethyldigallane, $Ga_2H_2(CH_3)_4$, by passing a mixture of methylgallium and hydrogen through a glow discharge. The methylgallane, which has an extrapolated b. p. of 172°, decomposes at 130° into methylgallium, gallium, and hydrogen. The gallium hydride is formed by allowing the methylgallane to react with triethylamine at a lower temperature. The following reaction occurs :

$$3Ga_2H_2Me_4 + 4NEt_3 = Ga_2H_6 + 4GaMe_3{\cdot}NEt_3$$

The molecular weight of the hydride corresponded with the formula Ga_2H_6. The b. p. (extrapolated) and m. p. were 139° and $-21{\cdot}4°$, respectively. It underwent decomposition into its elements at 130°.

A number of indium salts have been described by F. Ensslin and H. Dreyer.[13] These include the halides of In^{III}, the solubilities of which in water, expressed as g./100 g. of solution, are : InF_3 7·83, $InCl_3$ 64·7, $InBr_3$ 84·27, InI_3 91·6. Among a number of complex salts described, indium diethylthiocarbamate, $(NEt_2CS_2)_3In$, and indium hexamminocobaltic chloride, $In[Co(NH_3)_6]Cl_6$, are insoluble in acid solution and may be used for the determination of indium.

Amalgams of samarium, europium, and ytterbium have been described by J. K. Marsh [14] and H. N. McCoy.[15] Marsh prepared them by shaking the rare earths in acid acetate solution with dilute sodium amalgam. It was found that whereas samarium, europium, and ytterbium form amalgams, the cerium-group elements all show a lower power of amalgam formation, which decreases in order of atomic number. In the course of the experiments with europium amalgam evidence was obtained for the existence in solution of europous hydroxide with a solubility of at least 1 g./l. The use of the relative ease of amalgam formation exhibited by the rare-earth elements in effecting their separation was also studied.[16] Samarium could be extracted by amalgam formation from neighbouring elements, particularly neodymium and gadolinium, and fractional decomposition of the samarium amalgam gave a further means of purification, since this amalgam is relatively readily attacked by water or dilute acids. McCoy, who was concerned primarily with the preparation of amalgams, found that aqueous solutions of the acetates of europium and ytterbium in potassium citrate gave amalgams on electrolysis or on treatment with potassium amalgam. The solid amalgams $Hg_{10}Eu$ and Hg_2Eu_3 were prepared.

Further important publications on carbonyl chemistry by W. Hieber and his co-workers have appeared during the period under review.[17] Hieber has himself published an important review article.[18] The preparation of rhenium carbonyl halides has been described by W. Hieber, R. Schuh, and H. Fuchs.[19] The iodo-compound, $Re(CO)_5I$, is formed when carbon monoxide at 1 atm. is passed over a mixture of potassium hexaiodorhenate, K_2ReI_6, and copper powder heated to 200°. The bromo-compound is formed analogously at 200—300° and with a carbon monoxide pressure of at least 10 atm. To form rhenium carbonyl chloride a still higher pressure is needed. These compounds are also formed in good yield by the reaction of carbon monoxide on metallic rhenium mixed with a dissociable halide, *e.g.* (at 210 atm./250°)

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[12] E. Wiberg and T. Johannsen, *Angew. Chem.*, 1942, **55**, 38.

[13] *Z. anorg. Chem.*, 1942, **249**, 119.

[14] *J.*, 1942, 398.

[15] *J. Amer. Chem. Soc.*, 1941, **63**, 1622.

[16] J. K. Marsh, *J.*, 1942, 523.

$$Re + Cu(Hal)_2 + 6CO = Re(CO)_5(Hal) + Cu(Hal)CO$$

The carbonyl halides of rhenium diminish in volatility from the iodo- to the chloro-compound, and this is the order of increasing stability, since the iodo- is readily converted into the bromo-compound, or this into the chloro-compound, by the action of the appropriate free halogen.

These carbonyl halides are all very stable, and attempts to remove the halogen by such obvious means as the action of metallic silver were unsuccessful. It was also found impossible to prepare rhenium carbonyls directly from rhenium and carbon monoxide at high pressure. Rhenium pentacarbonyl was, however, obtained in good yield by the action of carbon monoxide at 200 atm. on the heptoxide, Re_2O_7, at 250°.[20] The carbonyl is a colourless crystalline substance which may be sublimed, and is soluble in organic solvents. It is also formed directly from potassium per-rhenate.

Cryoscopic measurements show rhenium carbonyl to be dimeric, though the carbonyl halides of the element are monomeric. The carbonyl is decomposed completely at 400°. Some indications were obtained of the existence of a carbonyl hydride of rhenium, but such a compound has not yet been isolated in a state of purity. Reaction of rhenium pentacarbonyl with amines was found to be comparable with that of the hexacarbonyls of the chromium group. In general, replacement of part of the carbon monoxide by co-ordinating amine groups occurs; *e.g.*, pyridine reacts at 240° according to the equation

$$[Re(CO)_5]_2 + 4Pyr = 2Re(CO)_3Pyr_2 + 4CO$$

With *o*-phenanthroline reaction occurs more readily and two molecules of carbon monoxide are replaced by one of the base. A similar replacement of part of the carbon monoxide occurs with the rhenium carbonyl halides, giving, *e.g.* $ReCl(CO)_3Pyr_2$ and $ReCl(CO)_3Phen$. R. Schuh[21] has published measurements of the extinction coefficients of rhenium carbonyl and of the carbonyl halides in solution.

Comparative data have been published on the formation of carbonyls of iron, cobalt, and nickel from their respective halides by the action of carbon monoxide at high pressure.[22] It is considered that in the synthesis of carbonyls by this method the ease of formation of the carbonyl increases with the ease of splitting off halogen from the metal, *i.e.*, in the order I > Br > Cl. Intermediate formation of carbonyl halides also occurs, a fact which explains the catalytic influence of iodine in the direct synthesis of carbonyls from metals and carbon monoxide. The rôle of copper or silver in these reactions is that of a halogen acceptor. Attempts to prepare iron carbonyl hydride by high-pressure synthesis gave only negative results.[23]

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[17] Cf. *Ann. Reports*, 1941, **38**, 71.

[18] *Angew. Chem.*, 1942, **55**, 7—11, 24—28.

[19] *Z. anorg. Chem.*, 1941, **248**, 243.

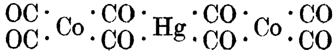
[20] W. Hieber and H. Fuchs, *ibid.*, p. 256.

[21] *Ibid.*, p. 276.

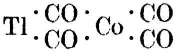
Important new mixed carbonyls containing cobalt have now been produced by the high-pressure method.[24] They are formed when either cobalt or an anhydrous cobalt halide, mixed with the metal in question, is treated at 200° with carbon monoxide at a pressure of 200 atm. The compounds so far prepared are of the following types : $M[Co(CO)_4]_2$, with M = Zn, Cd, Hg, Sn; $M[Co(CO)_4]_3$, with M = In, Tl; $M[Co(CO)_4]$, with M = Tl. Negative results were obtained with lithium, beryllium, magnesium, calcium, silver, gold, germanium, antimony, and bismuth. With lead, there was some indication of the formation of a mixed carbonyl.

These compounds are all volatile solids, soluble in indifferent organic solvents. The two thallium derivatives may be produced at will by employing the appropriate proportion of thallium in relation to the cobalt or cobalt halide. The mixed carbonyls are more stable than the dimeric cobalt tetracarbonyl. All are, however, decomposed by dilute acids to form cobalt carbonyl hydride and a salt of the second metallic component. The constitution proposed is illustrated in the case of the mercury and thallous derivatives by the formulæ (I) and (II).

(I.)



$$\begin{matrix}OC\cdot\\OC\cdot\end{matrix}Co\begin{matrix}\cdot CO\cdot\\\cdot CO\cdot\end{matrix}Hg\begin{matrix}\cdot CO\cdot\\\cdot CO\cdot\end{matrix}Co\begin{matrix}\cdot CO\\\cdot CO\end{matrix}$$



$$Tl\begin{matrix}\cdot CO\cdot\\\cdot CO\cdot\end{matrix}Co\begin{matrix}\cdot CO\\\cdot CO\end{matrix}$$

(II.)

Organometallic derivatives of iron carbonyls form yet another important new group of compounds described during the past year. The reaction of iron pentacarbonyl and iron carbonyl hydride with various organometallic compounds was first studied by F. Hein and H. Pobloth.[25] These experiments, which were made with derivatives of mercury, bismuth, thallium, and lead, gave for the most part very indecisive results, probably because of the instability of the products sought. A lead derivative of the formula $(C_2H_5)_2PbFe(CO)_4$ was, however, obtained by the interaction of triethyl-lead hydroxide and the calcium derivative of iron carbonyl hydride in presence of ether. The lead compound was a red crystalline substance which was soluble in organic solvents, was readily oxidised, and was decomposed above 130°. Subsequently the corresponding methylmercury iron tetracarbonyl, $(CH_3Hg)_2Fe(CO)_4$,[26] was described. It was obtained by decomposing aqueous methylmercury hydroxide covered with a layer of light petroleum with a solution of the calcium derivative of iron carbonyl hydride. The compound was insoluble in water but soluble in a variety of organic solvents. It could be sublimed in a vacuum but decomposed above 100° into dimethylmercury and mercury iron carbonyl.

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[22] W. Hieber, H. Behrens, and U. Teller, *Z. anorg. Chem.*, 1942, **249**, 26.

[23] W. Hieber and U. Teller, *ibid.*, p. 58.

[24] *Idem*, *ibid.*, p. 43.

[25] *Ibid.*, 1941, **248**, 84.

[26] *Idem*, *ibid.*, 1942, **249**, 293.

Evidence bearing on the supposed tautomerism of hydrogen cyanide has been obtained in an extension of earlier work on the synthesis of thiocyanates by the reaction of sulphur with organic cyanides.[27] It was argued that if hydrogen cyanide contained the tautomeric hydrogen *iso*cyanide the latter should react with sulphur to yield *iso*thiocyanic acid, HNCS, which would rearrange to form HSCN. This, in turn, should form the known degradation polymer $H_2C_2N_2S_3$. Sealed-tube experiments are recorded in which the reaction of liquid hydrogen cyanide with sulphur, selenium, and tellurium was studied, but they did not substantiate this reasoning. In the course of the work it was shown that the interaction of hydrogen cyanide with a mixture of pyridine or quinoline and sulphur or selenium yielded thiocyanates and selenocyanates of these bases. No tellurocyanates were isolated.

In a study of the cyanogen halides, P. Kailasam [28] found that bromine and dry cyanogen chloride react at room temperature to form a crystalline molecular compound, $3C_3N_3Cl,C_3N_3Br$. Cyanuric chloride reacts with 47% hydrogen bromide at room temperature, forming the compound $C_3N_3Cl_2Br$, which is soluble in organic solvents and is decomposed by water at 120°, giving cyanuric acid.

Silicon monoxide, the existence of which has hitherto been uncertain, has now been reinvestigated.[29] The oxide is best produced by heating silica or silicates with elementary silicon in a vacuum at 1450°. It is volatile under these conditions and, indeed, absorption bands associated with the vapour of SiO produced by reduction of silica with carbon at above 1500° were observed by N. F. Bonhoeffer in 1928.[30] Condensation of the vapour may give a finely-divided, yellow material, which so far has not yielded a characteristic *X*-ray diagram, or a glassy, brown solid. In either case analysis indicates the empirical formula SiO, but it is possible that a certain amount of disproportionation in the sense of the equation $2SiO \longrightarrow SiO_2 + Si$ takes place. The finely-divided, yellow condensate is pyrophoric. It reacts with water vapour at 500°, forming silica and hydrogen, and is capable of reducing metallic oxides.

An investigation of the iodides of silicon [31] has shown that purified silicon and iodine vapour react at 650°, forming the solid tetraiodide. When the latter is heated at 280° with a twofold excess of finely divided silver, Si_2I_6 and AgI result, but no indication is obtained of the existence of higher iodides. Disilicon hexaiodide when heated to 350—400° disproportionates into silicon tetraiodide and a polymeric monoiodide $(SiI)_n$, which appears to be similar to a monochloride described by R. Schwarz and U. Gregor.[32] It is believed to be a chain-like polymer with alternate single and double bonds between the silicon atoms. Hydrolysis of the monoiodide yields an ivory-coloured polymer which has the empirical formula $H_4Si_2O_3$ and is very readily oxidised. Thermal degradation of the latter in a vacuum leads to loss of hydrogen and the successive formation of the polymers $(H_3Si_2O_3)_n$ and $(H_2Si_2O_3)_n$. The final degradation product is a mixture of silica and silicon.

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[27] C. R. McCrosky, F. W. Bergstrom, and G. Waitkins, *J. Amer. Chem. Soc.*, 1940, **62**, 2031; 1942, **64**, 722.

[28] *Proc. Indian Acad. Sci.*, 1941, **14** *A*, 165.

[29] E. Zintl, W. Bräuning, H. L. Grube, W. Krings, and W. Morawietz, *Z. anorg. Chem.*, 1940, **245**, 1.

[30] *Z. physikal. Chem.*, **131**, 363.

[31] R. Schwarz and A. Pflugmacher, *Ber.*, 1942, **75**, 1062.

H. H. Anderson, in an extension of earlier work [33] in which cyanates and *iso*cyanates of silicon, phosphorus, and boron were prepared by the action of silver *iso*cyanate on the corresponding halides, has now described analogous derivatives of phosphorus oxychloride, and arsenic and antimony trichlorides. In addition, the corresponding thio-compounds $PO(SCN)_3$ and $As(SCN)_3$ were isolated.[34] The *iso*cyanates $PO(NCO)_3$, $As(NCO)_3$ and $Sb(NCO)_3$ were found to be volatile, but they isomerised when heated, forming the corresponding non-volatile cyanates.

An ammonia addition product of nitrogen tribromide, $NBr_3,6NH_3$, has been described by M. Schmeisser.[35] It is best prepared by mixing a stream of nitrogen carrying bromine vapour with an excess of ammonia in a vessel at 100°, in which ammonium bromide is deposited. The issuing gas stream, when passed through a trap cooled to $-95°$, deposits the red compound $NBr_3,6NH_3$. It was impossible to prepare nitrogen tribromide from the ammoniate because the latter exploded very readily. It was, however, shown that the ammoniate was soluble in methyl or ethyl alcohol, ether, or liquid ammonia, and that it could be recovered unchanged from the last solution.

The chemistry of quinquevalent bismuth compounds has been investigated by various authors in recent years. Well-authenticated derivatives of this valency state are comparatively few. Both potassium bismuth oxyfluoride [36] and bismuth pentafluoride [37] are of this type, and the recently prepared sodium orthobismuthate [38] is yet another example. The orthobismuthate is prepared by heating bismuth trioxide and sodium monoxide in air or oxygen at 650° :

$$Bi_2O_3 + 3Na_2O + O_2 = 2Na_3BiO_4$$

The product obtained with those proportions is free from sodium peroxide. The alternative method of oxidising bismuth salts to bismuthates in alkaline solution has been reviewed critically by R. Scholder and H. Stobbe,[39] who point out the great difficulty of obtaining all of the bismuth in the quinquevalent condition.

The preparation of thionylimide, SONH, by the interaction of thionyl chloride and ammonia has been described by P. W. Schenk.[40] Previously, F. Ephraim and H. Piotrowski,[41] by dropping thionyl chloride on liquid ammonia, had obtained a reaction which was represented by the equation

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[32] *Z. anorg. Chem.*, 1939, **241**, 1.

[33] *J. Amer. Chem. Soc.*, 1940, **62**, 761.

[34] *Idem, ibid.*, 1942, **64**, 1757.

[35] *Z. anorg. Chem.*, 1941, **246**, 284.

[36] O. Ruff, *ibid.*, 1908, **57**, 220.

[37] H. von Wartenberg, *ibid.*, 1940, **244**, 337.

[38] E. Zintl and K. Scheiner, *ibid.*, 1940, **245**, 32.

[39] *Ibid.*, 1941, **247**, 392.

$$2SOCl_2 + 7NH_3 = 4NH_4Cl + NH(SO{\cdot}NH_2)_2$$

A silver salt $NAg(SO{\cdot}NH_2)_2$ was isolated, and the same salt was obtained from the products of the interaction of sulphur dioxide and ammonia. Ephraim's work was repeated because it is known [42] that primary amines react with thionyl chloride according to the equation :

$$SOCl_2 + NH_2R = SONR + 2HCl$$

It was considered that a comparable reaction would occur with ammonia provided it were not present in excess.

The reaction was studied in the gas phase, the two reactants in stoicheiometric proportion being allowed to mix and the products being then cooled as rapidly as possible to the temperature of liquid air. Under these conditions the product was a colourless liquid, the analysis and molecular weight of which corresponded with the formula SONH. This compound melted at −85° and polymerised at temperatures above −70° to a yellow-brown, glassy resin.

Chromium tetrachloride has been prepared as an unstable brown solid by passing a stream of chlorine over the trichloride at 700° and cooling the issuing gas stream rapidly with a thimble containing solid carbon dioxide. The brown solid which condensed was analysed and had a composition approximating to $CrCl_4$. It has strong oxidising properties and was stable only below −80°.[43]

Chromic and cobaltic amides, $Cr(NH_2)_3$ and $Co(NH_2)_3$, are formed in the reaction in liquid ammonia solution between potassium amide and the hexammine nitrates of the respective elements.[44] Both the compounds are believed to be polymers. They react with ammonium salts in liquid ammonia solution, forming salts with a polymeric cation, of which the following were isolated :

$$[Br(NH_2)Cr(NH_3)_3]_nBr_n \qquad [NO_3(NH_2)Cr(NH_3)_3]_n(NO_3)_n$$
$$[(NH_2)_2Co(NH_3)_2]_n(NO_3)_n \qquad [NO_3(NH_2)CoNH_3]_n$$

Both amides react with excess of potassium amide in liquid ammonia, thereby exhibiting their amphoteric character. The following amphoteric amide derivatives were isolated :

$$[Cr(NH_2)_4]_nK_n\,;\ [NHCr(NH_2)_2]_nK_n\,;\ [Co_3N_2]_nK_n$$

Gaseous chlorine dioxide and fluorine have been shown to undergo a vigorous but non-explosive reaction when they are mixed at 0° and at low partial pressures in presence of a large excess of a diluent gas.[45] The compound ClO_2F was produced (m. p. − 115° ; b. p. − 6°). Though the reaction with water has not so far been elucidated, ClO_2F may be regarded as a fluoride of chloric acid. It is known to be very sensitive to reaction with water vapour, and is very much less liable to explode spontaneously than is chlorine dioxide. H. J. E.

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[40] *Ber.*, 1942, **75**, 94.

[41] *Ber.*, 1911, **44**, 379.

[42] A. Michaelis and O. Storbeck, *Annalen*, 1893, **274**, 187.

[43] H. von Wartenberg, *Z. anorg. Chem.*, 1942, **250**, 122.

[44] O. Schmitz-Dumont, J. Pilzecker, and H. F. Piepenbrink, *ibid.*, 1941, **248**, 175.

[45] H. Schmitz and H. J. Schumacher, *ibid.*, 1942, **249**, 238.

2. Luminescence of Inorganic Solids.

The study of the phenomena of fluorescence and phosphorescence of inorganic solids has become so extensive that any attempt to review the field as a whole would be impossible here, but the increasing industrial applications and the advances in the theoretical interpretations of these phenomena warrant a report of the recent work on selected aspects of it. The work before 1928, carried out mainly on alkaline-earth phosphors by Lenard and his collaborators, has been recorded comprehensively,[1] and the luminescence of incandescent solids was the subject of a report from the Carnegie Institute of Washington in the same year.[2] Neither of these types of phosphor will be reviewed here, as the more important advances in recent years have been made with other luminescent solids. Various aspects of the field were discussed by the Faraday Society in 1937.[3]

Luminescent inorganic solids can be broadly classified according as to whether the emission takes the form of (i) discrete or line spectra, or (ii) continuous spectra, where the broad bands persist as bands even at low temperatures. F. H. Spedding [4] has recommended low-temperature investigation as a method of establishing the class. For the purposes of this Report, a chemical classification will be employed, broadly separating these materials into pure and impurity-activated compounds, and specifically classifying them according to chemical constitution. It is by no means possible to apply any theoretical interpretation applicable to one class of phosphors to another class, and each case must be considered individually.

Mechanism of Luminescence of Solids.—As far as has been investigated, luminescent properties appear to be extremely dependent on structure, and strong luminescent properties are associated with defects in the crystal lattice. The more ideal crystals investigated do not appear to luminesce to the same extent as those containing more lattice defects. H. W. Leverenz and F. Seitz [5] consider it possible that truly ideal crystals are not luminescent under ultra-violet or cathode-ray excitation. Pure crystalline compounds are in general far from ideal and the defects may arise in several ways: (i) Ions of either type may be absent from the lattice. These vacancies are caused by diffusion into the body of the lattice of holes present in the surface of the crystal. Heating these crystals causes a considerable increase in the number of these vacancies. (ii) In other lattices, particularly where the structure is open, excess metal atoms or metal-impurity atoms may occupy interstitial positions. (iii) In others, ions may diffuse from normal lattice positions into interstitial positions, leaving vacancies. These crystals then have both types of defect present in the lattice. It can be seen that impurity atoms may take up positions in any of these lattices, provided they be not prevented from doing so by their size.

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[1] "Handbuch der Experimentalphysik," 1928, **23**.

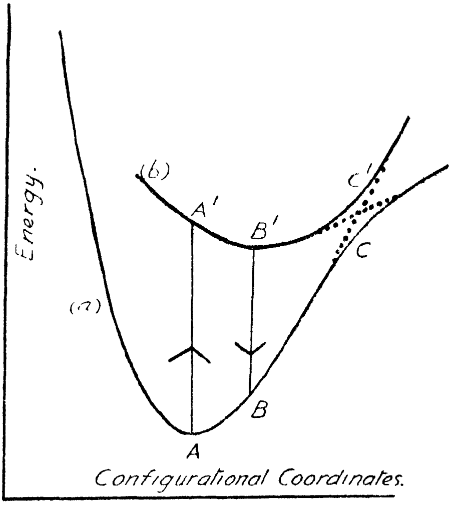
[2] E. L. Nichols, H. L. Howes, and D. T. Wilkins, Publ. No. 384, 1928.

[3] General Discussion on Luminescence, 1939.

[4] *Trans. Faraday Soc.*, 1939, **35**, 65.

[5] *J. Appl. Physics*, 1939, **10**, 479.

According to the modern theory of solids,[6] allowed energies of atoms and ions are not single energy levels but are energy ranges or bands. This modification of the ionic levels is due to the presence of the crystal lattice, and it is possible to trace back the bands to the energy levels of the free atom or ion. In ideal insulating crystals these bands are separated by forbidden regions, the lower band of levels being filled and the upper band empty. The implications of this, *viz.*, that the lowest-energy ultraviolet absorption band should correspond to excitation of electrons from the filled band to the empty band, and the consequent photoconductivity due to ionisation, were not fulfilled by experiment. In the alkali halides,[7] for instance, the lowest-energy spectral absorption bands were narrow, and photoconductivity did not occur on absorption. These bands correspond to so-called "excitation levels," just below the unfilled ionisation band. These levels have been ascribed to the energies of electrons which have remained associated with their positive holes due to Coulomb attraction after excitation.



*Potential-energy curves for normal and excited states in a crystal lattice.**

Imperfect pure crystals usually have extra levels (" centre " levels) by virtue of their lattice defects. In certain alkali halide phosphors these extra levels give rise to the *F*- or colour bands in the visible spectral region, these being associated with a stoicheiometric excess of alkali metal in the lattice. Lattice defects caused by the presence of impurity atoms in interstitial positions also result in similar energy levels between the lower filled and the upper empty energy bands.[8]

The luminescent process has been illustrated by use of diagrams representing the energy of the lattice as a function of the atomic displacement from equilibrium positions.[9] The transition AA', corresponding to absorption, raises the lattice to an upper vibrational level of the higher electronic state. Apart from resonance radiation by the transition $A'A$, the vibrational energy of the excited state is dissipated without optical emission, the equilibirum position B' being attained. The transition $B'B$ may then take place with the emission of light of lower energy, and therefore longer wavelength, than the exciting radiation. Excitation of phosphors in the absorption bands due to the " centre " levels [5] is always more efficient in the production of luminescence than excitation in the strong fundamental band; furthermore, excitation in either band causes the same luminescent emission. The explanation of this has been given by F. Seitz.[10] Excitation at an impurity or lattice defect centre induces luminescence of the type discussed above, whereas excitation in the fundamental band induces photoconductivity, as the electrons have been excited into the ionisation bands. These electrons transfer their energy to the impurity or defect centres, after which radiation is emitted according to the above mechanism. Another concept which is necessary for the comprehension of certain aspects of luminescence is that of trapping levels, *i.e.*, metastable states in which energy may be trapped for some time before thermal agitation brings the system into a condition for luminescent emission again. If the functions representing the energy levels approach closely at some point C, then a probable mechanism for the dissipation of energy is the thermal excitation to a vibrational level at C', at which point the transition to the lower level and immediate dissipation of the excess vibrational energy now possessed brings the lattice to the equilibrium state without optical radiation. Such a mechanism accounts for the quantum efficiencies of luminescence less than unity and also for decrease of luminescence at temperatures above normal.

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[6] F. Seitz, " Modern Theory of Solids," McGraw-Hill, 1940.

[7] R. Hilsch and R. Pohl, *Z. Physik*, 1928, **48**, 384.

[8] N. Riehl, *Ann. Physik*, 1937, **29**, 663.

[9] R. W. Gurney and N. F. Mott, *Trans. Faraday Soc.*, 1939, **35**, 69.

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Certain luminescent materials show an after-glow lasting for minutes, hours, or even days in certain cases and microseconds in others. The distinction between the phenomenon of fluorescence and that of phosphorescence is quite arbitrary in practice, as any fluorescent emission must take place at a finite time after the excitation process. P. Pringsheim [11] has proposed that the term *fluorescence* be reserved for processes of emission involving inner transition probabilities, whilst the term *phosphorescence* should be applied to processes in which metastable states are involved. The distinction between these processes can be made by considering the decay law which the after-glow follows, and the temperature-dependence of the process. This involves previous knowledge of the decay process, but is nevertheless the only logical way of defining the terms.

In the previous section we have seen that absorption of energy in impurity-activated phosphors may result in the excitation of electrons to the conduction band or to levels in the impurity centres without ionisation. In either process the subsequent emission is due to the transition from an excited un-ionised state to the ground state in the impurity centre. The process is, of course, accompanied by a loss of energy by thermal vibrations in the lattice. In the case of phosphors not exhibiting photo-conductivity the decay law is simply $I = I_0 e^{-\alpha t}$, where I is the intensity of the phosphorescence at a time t after the removal of the excitation, when the intensity was I_0 ; α is the decay constant, the order of which depends on the probability of the transition from the excited to the ground state. It is expected that α should have a small temperature dependence. In the case where photoconductivity occurs, and even in certain cases of excitation to impurity levels, however, the electron must recombine with one of the centres which has lost an electron and a bimolecular type of law results, *viz.*, $I = I_0/(1 + \alpha t)^2$; α here exhibits a strong temperature dependence. These two laws represent the simplest cases of the decay process, and most experimental determinations reveal a superposition or modification of these processes.

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[10] *Trans. Faraday Soc.*, 1939, **35**, 74.

[11] *Ibid.*, p. 87.

A. L. Reimann[12] found experimentally that the photoconductivity of zinc sulphide phosphors at −196° decays slowly under the influence of infra-red radiation and after the excitation has been removed. The law governing this decay is $\sigma = \sigma_0/(1 + \alpha t)$, where σ is the conductivity after a time t and σ_0 that at $t = 0$. This is in agreement with the bimolecular decay law, as the conductivity is proportional to the number of free electrons.

Preparative Methods.—In all preparations of luminescent materials the utmost purity is essential, and in the case of impurity-activated materials small and controlled amounts of particular elements must be added. The reasons for this will be apparent in later discussion, as the presence of certain foreign ions causes marked diminution in the efficiency of the luminescence, even to the extent of its complete suppression. The characteristics of the luminescence are strongly dependent on the activator and its concentration. Furthermore, the emission characteristics are governed considerably by the conditions of preparation. In certain cases where the crystal exists in more than one modification the temperature of preparation and the conditions of quenching are important.

In the subsequent matter, attention will be directed to the more important aspects of the preparation and the spectral characteristics of the members of the various classes of phosphors.

Alkali Halide Phosphors.—Alkali halide crystals which are ideal do not luminesce to any extent, but when lattice defects are introduced, luminescence can be induced by irradiation in certain ultra-violet regions. Alkali halide crystals containing stoicheiometric excess of either alkali metal or halogen exhibit new absorption bands in the visible (*F*-bands) and the ultra-violet, respectively.[13] Irradiation in the *F*-bands is claimed to cause fluorescence and phosphorescence. Sodium chloride containing *F*-centres, when irradiated with λ 4700 (the maximum of the *F*-band), emits fluorescent and phosphorescent light of the same spectral distribution as the *F*-band.[14] However, H. W. Leverenz and F. Seitz[5] consider that the results are inconclusive. Investigations into those alkali halides in which thallium, bismuth, silver, copper, or lead have been incorporated into the vacancies in the alkali-metal ionic lattice, have been carried out mainly by R. Pohl, R. Hilsch, and their co-workers.[15] Activators are added as chlorides or nitrates of the impurity element to the alkali halide to the extent of 10^{-3} or 10^{-4} mol. %. They may be added to the melt or electrolytically diffused into the lattice at temperatures above 350°. The presence of the activator gives rise to new absorption bands on the long-wave-length side of the characteristic absorption of the pure alkali halide.[16] By far the most satisfactory case from experimental and theoretical points of view is that of the thallium-activated series, as here it has been conclusively shown that the thallium is monatomically dispersed throughout the lattice,[16] whereas those activated by lead or silver, for instance, appear to occur in the halide lattice as complex molecular groups. The mechanism of the absorption and emission processes has been satisfactorily established by F. Seitz[17] for the former case. The three absorption peaks due to the impurity atoms are situated at λ 1990, λ 2160, and λ 2550 and are invariant with the alkali halide used. The absorption peaks have been associated with the electronic transitions $^1S_0 \longrightarrow {}^3P_1$, $^1S_0 \longrightarrow {}^3P_2$, and $^1S_0 \longrightarrow {}^1P_1$ in the free thallium ions, modified by the perturbations introduced by the lattice field. Transitions of this type preclude ionisation and hence photoconductivity, a condition which is supported by experiment. The two emission bands in the near ultra-violet and visible in KCl–Tl, for instance, are observed in all cases and appear to be due to the transitions $^1S_0 \longleftarrow {}^3P_1$ and $^1S_0 \longleftarrow {}^3P_0$ from the lowest vibrational levels of $^3P_1$ and $^3P_0$ to higher vibrational levels of $^1S_0$. Excitation to the $^1P_1$ level by absorption in the band at λ 1990 causes fluorescent emission of the same bands as excitation in either $^3P_1$ or $^3P_2$ This is explained by Seitz in terms of a number of radiationless transitions of the type described and illustrated in the figure. Phosphorescence, however, occurs only after the excitation $^1S_0 \longrightarrow {}^1P_1$, and the existence of a metastable state associated with the $^1P_1$ band must be postulated. Vibrational energy must be supplied before the thallium ion can jump to the triplet states, from which phosphorescent emission of the same nature as the fluorescent emission can occur. The metastable state occurs only when the absorbing thallium ion has another thallium ion among its nearest neighbours.

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[12] *Nature*, 1937, **140**, 501.

[13] See R. Pohl, *Physikal. Z.*, 1938, **39**, 36.

[14] See E. Hirschlaff, "Fluorescence and Phosphorescence," Methuen, 1938.

Cathode-ray bombardment can also excite these phosphors to fluorescence, but they are unstable under such treatment.[5]

Zinc Sulphide and Related Phosphors.—Sulphides of zinc and cadmium and their solid solutions have emission spectra which consist in general of one, or in some cases two broad bands in the visible region, the position of the bands being dependent on the activating impurity and to some extent on its concentration. These sulphides are liable to exhibit lattice defects in view of the open type of lattice which they possess, foreign ions being capable of homogeneous penetration into the interstices of the lattice by diffusion processes at elevated temperatures. N. Riehl[18] has found that copper, silver, gold, and manganese could activate the lattice by taking up interstitial positions, whereas larger atoms such as those of lead and bismuth, which cannot penetrate the lattice, show no activation. Pure zinc sulphide may be activated by heating to high temperatures, the zinc ions diffusing into interstitial positions to produce lattice defects. The mobility of other activators such as copper appears to be much greater than that of the lattice ions themselves, as copper can be incorporated by lattice diffusion, irrespective of surface diffusion, at temperatures as low as 330°.[19]

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[15] See R. Hilsch, *Proc. Physical Soc.*, 1937, **49**, (extra part) 40, for references to experimental work.

[16] W. Koch, *Z. Physik*, 1929, **57**, 638.

[17] *J. Chem. Physics*, 1938, **6**, 150; *Trans. Faraday Soc.*, 1939, **35**, 74.

The preparative methods are merely means of facilitating these processes. Although the rôle of the flux employed is rather indefinite, particularly in the case of the alkaline-earth sulphides, its presence in the pure zinc sulphide has been shown not to affect the luminescence.[20] A comparative investigation into the known preparative methods has been conducted by N. F. Zhirov,[21] and W. H. Byler[22] has studied the effect of factors such as particle size, time and temperature of heating, and foreign ion content on the activation by heat treatment, and has established a correlation with the luminescence. S. Makishima[23] directed attention to the quenching conditions and the use of fluxes. The patent literature on preparative methods is extensive. Those of interest are (i) explosion of powdered zinc and sulphur together with flux and activator in an atmosphere of nitrogen at 3000°,[24] (ii) activation of commercial zinc sulphide by prolonged electron bombardment,[25] (iii) incorporation of the activator by cathode sputtering in a high vacuum.[26]

The spectral absorption of zinc sulphide has been the subject of much discussion. The fundamental band due to the zinc sulphide matrix appears to have a maximum below λ 2500 and a long-wave-length limit at λ 3350, as measured by J. H. Gisolf[27] and J. A. Kitchener.[28] However, Seitz,[29] quoting unpublished measurements by H. W. Leverenz, and F. A. Kröger[20] point out that activated zinc sulphide has its maximum excitation beyond this limit at λ 3600, and that a less pronounced absorption is present in this region, ascribed by Seitz to the interstitial atom. The emission bands are characteristic of the activator. With small activator concentrations, the band due to ZnS–Zn may appear together with that due to the foreign impurity centres, unresolved in the case of ZnS–Ag, but noticeable as a "hump" on the long-wave-length side,[30] and resolved in the case of ZnS–Cu. The appearance of the band depends on the activator concentration and on the heat treatment in the preparation, for under certain conditions diffusion of foreign ions into interstitial positions may take place without the movement of zinc ions within the lattice.[18] This probably explains the appearance of only one band at λ 5400 in some cases of ZnS–Cu and two, at λ 4600 and λ 5400, in others. The emission band ascribed by C. J. Milner [30] to ZnS–Pb is in direct contradiction to experiments by N. Riehl [18] on the diffusion of ions in zinc sulphide. Milner's emission band has its maximum at λ 4600 and is no doubt due to ZnS–Zn. Furthermore, owing to the difficulty in excluding minute activating traces during preparation, most zinc sulphides possess weak bands due to these other impurities. This is particularly noticeable in specimens of ZnS–Ag, which invariably have a green component due to copper. J. H. Gisolf and F. A. Kröger [31] have shown that this becomes particularly apparent owing to differential behaviour with variation of temperature and intensity. Cadmium sulphide behaves similarly to zinc sulphide, its fundamental absorption having a long-wave-length limit at λ 5165, but the emission band has its maximum in the infra-red, although this band does extend into the red.

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[18] *Ann. Physik*, 1937, **29**, 640; *Trans. Faraday Soc.*, 1939, **35**, 135.

[19] E. Tiede and E. Weib, *Ber.*, 1932, **65**, 371.

[20] F. A. Kröger, *Physica*, 1940, **7**, 1.

[21] *J. Appl. Chem. U.S.S.R.*, 1934, **7**, 343.

[22] *J. Amer. Chem. Soc.*, 1938, **60**, 632.

[23] *J. Soc. Chem. Ind., Japan*, 1938, **41**, 202.

[24] Fr. P. 685,768, 745,644.

[25] D. R.-P. 605,969; B.P. 407,540.

[26] B.P. 414,597.

[27] *Trans. Faraday Soc.*, 1939, **35**, 94.

[28] *Ibid.*, p. 97.

[29] *Ibid.*, p. 99.

[30] *Ibid.*, p. 101.

Solid solutions of zinc and cadmium sulphides have intermediate characteristics depending almost linearly on the molar composition of the mixture, and do *not* show two separate bands which vary in their relative intensity according to the composition.[32] F. A. Kröger [20] investigated the system of these two sulphides thoroughly, and found that a new group of absorption and emission bands appeared at −180°, the position and separation of these bands varying with the molar composition in the same way. He also studied the absorption and luminescence of ZnS–MnS and ZnS–CdS–MnS systems [33] and found in absorption a fundamental characteristic of the ZnS or ZnS–CdS and a band system characteristic of the MnS.

The phosphorescence of these compounds decays according to a bimolecular law, which is readily understood from the existence of photoconductivity under excitation which also produces luminescence.[34, 35] The existence of metastable states, or " trapping " levels, rather complicates the process, but is nevertheless necessary to explain the long-duration phosphorescence. An investigation by W. de Groot [34] on ZnS–Cu has led to some interesting conclusions. He found a rapid decay at high intensities of exciting radiation, as predicted by the decay law, and also with radiation of shorter wave-length. The latter he ascribed to the fact that such radiation is absorbed in a thin layer of material, and the resultant intensity of radiation per unit volume of luminescing material is consequently greater. J. W. Strange [36] reports that zinc sulphide phosphors activated by silver and copper show two short-period decays of an exponential character when excited by cathode rays. At high current densities a component of about 1 microsecond decay was observed, whereas at low current densities another component of about

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[31] *Physica*, 1939, **6**, 1101.

[32] J. H. Gisolf, *ibid.*, p. 84.

[33] *Ibid.*, p. 779; 1940, **7**, 92.

[34] W. de Groot, *ibid.*, 1939, **6**, 275, 393.

[35] W. L. Levshin and W. W. Antonov-Romanovsky, *Physikal. Z. Sowjetunion*, 1934, **5**, 769; W. W. Antonov-Romanovsky, *ibid.*, 1935, **7**, 366; *Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **2**, 97.

[36] *Trans. Faraday Soc.*, 1939, **35**, 95.

50 microseconds decay predominates. L. A. Levy and D. W. West [37] record the quenching of the X-ray phosphorescence of zinc sulphide by 1 part of nickel in 10^6 without influence on the fluorescence. This result has led to some interesting discussion as to its cause,[3] but no completely satisfactory explanation has yet appeared.

Silicate Phosphors.—Extensive publications have been made on the properties of zinc orthosilicate, Zn_2SiO_4, both pure and activated, and also of a so-called zinc metasilicate, $ZnSiO_3$. Reference to the $ZnO–SiO_2$ phase diagram [38] shows that the latter compound does *not* exist, the only compound being the orthosilicate : papers purporting to deal with $ZnSiO_3$ are, in fact, considering Zn_2SiO_4 with excess SiO_2. The pure orthosilicate, however, exists in three modifications, α, the normal modification formed by slow cooling of the melt, and the β- and the γ-form obtained by rapid quenching of the melt. The last two forms revert to the α-form on heating to 900° and 300° respectively.[39] Non-activated zinc silicate phosphors may be prepared in these three varieties—fluorescing green, yellow, and red, respectively. G. R. Fonda [40] considers the yellow variety to be an amorphous complex of zinc oxide and silica in orthosilicate proportions, and the red phosphor a similar amorphous complex in the proportions ZnO,SiO_2. Although Fonda claimed that the only crystalline phases of the yellow modification were cristobalite and zinc oxide, H. P. Rooksby and A. H. McKeag[41] and S. H. Linwood and W. A. Weyl,[42] in agreement with A. Schleede and A. Gruhl,[39] have produced X-ray evidence for a second crystalline modification of zinc orthosilicate, which appears to be derived from the cristobalite modification of silica. The red phosphor, prepared by rapid quenching from high temperatures, was reported by Schleede and Gruhl to be crystalline, although the X-ray evidence was by no means conclusive. Rooksby and McKeag failed to obtain any evidence of a third crystalline modification, and Linwood and Weyl are of the opinion that it is a true glass.

The α-orthosilicate absorbs in the range $\lambda\lambda$ 2200–3000 [43] and also appears to be excited to luminescence by the neon resonance lines λ 736 and λ 740.[44] A. Rüttenauer [44] has demonstrated that λ 3650 also produces luminescence. In an attempt to correlate these facts, F. A. Kröger [45] has studied the absorption, excitation, and emission spectra of zinc silicate phosphors. The introduction of manganese was not found to shift the absorption edge, but increased the absorption on the long-wave-length side. A new series of bands with a new edge at λ 3000 appeared in compositions containing more than 5% of manganese. In emission, pure *α-orthosilicate has a maximum at* λ 4150, minute additions of manganese developing a new band in the green at λ 5230. With further increase above 5% of manganese a red band developed with a maximum at λ 6100.

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[37] *Trans. Faraday Soc.*, 1939, **35,** 128.

[38] E. N. Bunting, *J. Res. Nat. Bur. Stand.*, 1930, **4,** 131.

[39] *Z. Elektrochem.*, 1923, **29,** 411.

[40] *J. Physical Chem.*, 1940, **44,** 851.

[41] *Trans. Faraday Soc.*, 1941, **37,** 308.

[42] *J. Opt. Soc. Amer.*, 1942, **32,** 443.

[43] C. G. Found, *Trans. Ill. Eng. Soc.*, 1938, **33,** 186; J. W. Marden, N. C. Beese, and G. Meister, *ibid.*, 1939, **34,** 65.

[44] A. Rüttenauer, *Z. tech. Physik*, 1938, **14,** 31; H. G. Jenkins and J. N. Bowtell, *Trans. Faraday Soc.*, 1939, **35,** 155; M. Schön, *ibid.*, p. 162; G. R. Fonda and H. Huthsteiner, *J. Opt. Soc. Amer.*, 1942, **32,** 156.

[45] *Physica*, 1939, **6,** 764.

Taken in conjunction with J. T. Randall's work on manganese-activated phosphors,[46] this work leads to one conclusion, *viz.*, that these bands are due to the bivalent manganese ion in different lattice environments. It is to be noted that substitution of some of the zinc by beryllium also leads to the development of the red band. S. H. Linwood and W. A. Weyl,[42] in their experiments on fluorescent glasses activated by manganese, found evidence that the green band is associated with manganese ions in the lattice positions, whereas the red band is attributed to transitions involving these ions in interstitial positions. They consider that these conclusions may be applied to the crystalline silicates also. The double silicates of zinc with titanium, zirconium, hafnium, and thorium produce emission bands in the violet. In zinc beryllium silicates with additions of Group IV silicates the red band is retained also, the consequent phosphors corresponding to almost white colours.[5]

The phosphorescence of silicate phosphors has been studied by G. R. Fonda,[47] N. C. Beese,[28] and K. Birus and H. Zierold.[49] The decay law for the green band in manganese-activated silicate phosphors was found to be complex, the first process being an exponential decay unaffected by temperature, and the second a temperature-dependent bimolecular process.

A completely satisfactory mechanism for the luminescence of silicates has not yet been advanced, but any proposed mechanism must take into account the decay process and the photoconductivity.[50]

Tungstates and Molybdates.—Pure tungstates and molybdates of bivalent metals such as calcium, magnesium, zinc, and cadmium are luminescent under cathode ray and ultra-violet excitation.[51] The emitted light is a broad band in the blue region of the spectrum, which appears to be independent of any trace elements which may be present, except that rare-earth ions, such as those of samarium and europium, may cause the appearance of new bands.[52] Small concentrations of lead have been claimed as enhancing the luminescence of calcium tungstate although no appreciable shift occurs in the spectrum.[53] No mechanism for the emission process has yet been advanced, as little physical investigation has been done on these phosphors. There is no long afterglow in the case of tungstate phosphors, as in the phosphors already mentioned, but it is of the order of 10^{-5} sec.,[36] and this makes any interpretation on the basis of mechanisms suggested for other phosphors precarious.

[46] *Trans. Faraday Soc.*, 1939, **35**, 11; *Nature*, 1938, **142**, 113; *Proc. Roy. Soc.*, 1939, *A*, **170**, 272.

[47] *J. Appl. Physics*, 1939, **10**, 408.

[48] *J. Opt. Soc. Amer.*, 1939, **29**, 26.

[49] *Naturwiss.*, 1942, **30**, 63.

[50] R. Hofstadter, *Physical Rev.*, 1938, **54**, 864.

[51] A. Schloemer, *J. pr. Chem.*, 1932, **133**, 51.

[52] M. Servigne, *Tech. Moderne*, 1937, **29**, 443; *Compt. rend.*, 1935, **200**, 2015.

[53] F. E. Swindells, *J. Opt. Soc. Amer.*, 1933, **23**, 129.

Miscellaneous Luminescent Materials.—Numerous other compounds have been reported as exhibiting visible luminescence from time to time. It would be impossible even to list them here, but some of the more interesting classes are: borates of cadmium and zinc activated by manganese (red luminescence); phosphates of zinc, activated by manganese (red);[46] magnesium titanate (red);[54] beryllium nitride (blue);[55] and the chromium-activated phosphors of alumina.[56]

A. L. G. R.

3. SOME APPLICATIONS OF MODERN TECHNIQUE IN INORGANIC CHEMISTRY.

A number of recent contributions to Inorganic Chemistry lend themselves particularly well to discussion from the viewpoint of experimental technique, and illustrate the important advances made possible by the development of new methods of investigation. It is generally recognised that the introduction of vacuum methods of manipulation by Stock and others was the key to the chemistry of volatile hydrides, and many recent advances in Inorganic Chemistry have similarly been initiated by the development of new technique.

A general trend of considerable importance is evident in the increasing amount of work being carried out on solid substances and their reactions. This trend is attributable to the more widespread availability of X-ray methods for examination of crystalline materials. Since X-radiograms afford information on the actual lattice structure of a solid, they provide a powerful method of general application for identifying and characterising crystalline substances. Although the more refined methods of X-ray crystallography, applied generally to single crystals, are needed for the elucidation of structural details, powder X-radiograms obtained by the Debye–Scherrer method are eminently suitable for routine use in identifying a solid material or establishing its homogeneity. It is important that the potentialities of X-ray methods in ordinary research work on Inorganic Chemistry should be more widely recognised, and for this reason some prominence is given to such methods in this Report.

A typical instance of the utility of X-ray powder analysis is afforded by a recent paper on the structures of heavy-metal iron cyanides,[1] in which Prussian-blue and Turnbull's blue, long thought to be distinct compounds, are shown to be chemically identical. A distinction between the formulæ $Fe_4[Fe(CN)_6]_3$ (ferric ferrocyanide) and $Fe_3[Fe(CN)_6]_2$ (ferrous ferricyanide) cannot be made from the X-ray data, but the latter formula is supported by oxidation–reduction potential measurements.

In the study of different modifications of polymorphic solids, X-ray methods are invaluable, since they permit unequivocal identification of the individual modifications, even in specimens differing in their state of division, or containing impurities. The formation of different crystalline forms of calcium carbide in the electric arc furnace has recently been studied[2] with the aid of *X*-ray powder technique. "CaC_2 III," the form which reacts most readily with nitrogen in the formation of calcium cyanamide, is obtained directly from calcium carbonate and carbon in the arc furnace if nitrogen and sulphur are carefully excluded; grinding of the product readily causes transformation into another known form, "CaC_2 II." A new form of the carbide, "CaC_2 IV," stable only at high temperatures, was identified through the use of a Debye–Scherrer camera designed for examination of powder samples held at temperatures up to 600°. The use of *X*-ray technique in this investigation has permitted a detailed and direct study of the interrelationships of the different forms of calcium carbide.

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[54] E. Tiede and E. Villain, *Ber.*, 1940, **73**, 274.

[55] S. Satô, *Bull. Inst. Phys. Chem. Res., Japan*, 1935, **14**, 920.

[56] O. Deutschbein, *Ann. Physik*, 1932, **14**, 712; 1939, **20**, 828; *Physikal. Z.*, 1932, **33**, 874.

[1] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Physical Chem.*, 1942, **46**, 99.

Non-stoicheiometric compounds have recently received considerable attention, and the applicability of *X*-ray analysis in this field is well illustrated by a paper on lower vanadium oxides.[3] A "VO-phase" is found to be stable in the composition range $VO_{0{\cdot}9}$—$VO_{1{\cdot}3}$ at high temperatures; on cooling, this phase decomposes into vanadium (or a solid solution of oxygen in vanadium) and a higher oxide of undetermined constitution. The "V_2O_3-phase" has a lower limit of stability at the approximate composition $VO_{1{\cdot}35}$.

In the examination of systems in which a number of solid phases may occur, *X*-ray methods have led to marked advances. Recent work includes a study of magnesium amalgams,[4] in which the existence of compounds having the formulæ Mg_3Hg, Mg_5Hg_2, Mg_2Hg, Mg_5Hg_3, MgHg, and $MgHg_2$ was established. Reference may also be made to a detailed examination of hydrated forms of cupric oxide, and of certain basic copper sulphates,[5] in which previous conflicting conclusions were resolved by *X*-ray analysis and by isothermal or isobaric dehydration experiments. $Cu(OH)_2$ was found to be the only compound formed in the system $CuO–H_2O$, and in the portions of the system $CuO–SO_3–H_2O$ which were studied the stable solid phases were found to be $4CuO,SO_3,3H_2O$ and a new basic sulphate, $5CuO,SO_3,nH_2O$. In further work on the system $Na_2O–SiO_2–P_2O_5$ Debye–Scherrer *X*-radiograms have shown that anhydrous sodium silicophosphates do not occur as stable solid compounds.[6]

Some attention has been given recently to techniques involving sintering of powder mixtures, recent work on the theory of reactions between solids having led to renewed interest in processes of this type, which are of considerable practical importance. The theoretical and experimental basis of the subject has been reviewed in detail by G. F. Hüttig,[7] by whom much of the original work in this field has been carried out. W. Jander and his collaborators have also continued their studies on "intermediate states" in reactions between solid oxides.[8] The formation of these states is shown by changes in the catalytic activity, adsorptive power, rate of dissolution, and other properties of the oxide mixtures after controlled heat treatment, and their investigation has contributed considerably to our knowledge of the changes involved in reactions between powdered materials. A brief outline of Jander's views on these changes, in which Hüttig's slightly different approach is explained, has appeared recently.[9] Several reactions between powdered solids at temperatures well below their melting points, particularly reactions involving arsenic trisulphide and metallic oxides, have been studied by E. Montignie.[10] Other instances of sintering reactions include the preparation of several alkali–alkaline earth phosphates from stoicheiometric mixtures of the alkali carbonate with the alkaline earth monohydrogen phosphate (*e.g.*, $NaSrPO_4$ is obtained from Na_2CO_3 and $SrHPO_4$).[11] Preparation of a cadmium apatite, $Cd_{10}(PO_4)_6F_2$, and of certain mixed calcium cadmium apatites (the corresponding Ca_9Cd, Ca_5Cd_5, and $CaCd_9$ compounds) by heating appropriate mixtures of calcium and cadmium phosphates and fluorides is also reported.[12]

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[2] M. A. Bredig, *J. Physical Chem.*, 1942, **46**, 801.

[3] W. Klemm and L. Grimm, *Z. anorg. Chem.*, 1942, **250**, 42.

[4] G. Brauer and R. Rudolph, *ibid.*, 1941, **248**, 405. Fig. 1 on p. 406 of this paper shows particularly well how the existence of the various solid phases can be deduced from the *X*-radiograms.

[5] H. B. Weiser, W. O. Milligan, and E. L. Cook, *J. Amer. Chem. Soc.*, 1942, **64**, 503.

[6] E. Zintl and W. Morawietz, *Z. anorg. Chem.*, 1940, **245**, 12.

In spite of the general trend towards the chemistry of solids, little work has been published recently on reactions at temperatures above the limit of approximately 1000° attainable with common laboratory furnaces. Although the use of temperatures much above this limit incurs difficulties with both heating elements and refractory materials, the construction of suitable furnaces is not outside the range of the average laboratory.[13] Some of the most interesting recent high-temperature studies are those of E. Zintl and his collaborators on the monoxides of boron and silicon,[14, 15] referred to elsewhere in this Report.[16] An interesting development due to Zintl is the use of elemental silicon as a reducing agent at high temperatures. For instance, metallic niobium of 99% purity is obtained by heating the dioxide, NbO_2, with the stoicheiometric quantity of silicon at 1800°; the silicon and oxygen form silicon monoxide, which volatilises. Silicon monoxide itself appears to have useful reducing properties; metallic magnesium distils from a mixture of calcined dolomite, lime, and silicon monoxide heated at 1350° ($MgO,CaO + CaO + SiO = Ca_2SiO_4 + Mg$), and zinc is similarly obtained from zinc oxide or a calcined zinc ore at 1200—1300°. In discussing the use of silicon as a reducing agent, Zintl points out that silicides formed as intermediate products in the reduction process are likely to be more readily decomposed than corresponding carbides, so that silicon may be preferable to carbon as a reducing agent in certain cases.[15]

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[7] *Kolloid-Z.*, 1941, **94**, 137; **95**, 258; **97**, 281; 1942, **98**, 6, 263. Other recent papers by Hüttig *et al.* on sintering in metallic powders are as follows: G. F. Hüttig, C. Bittner, R. Fehser, H. Hannawald, W. Heinz, W. Hennig, E. Herrmann, O. Hnevkovsky, and J. Pecher, *Z. anorg. Chem.*, 1941, **247**, 221; J. Hampel, *Z. Elektrochem.*, 1942, **48**, 82; G. F. Hüttig and K. Arnestad, *Z. anorg. Chem.*, 1942, **250**, 1.

[8] W. Jander and G. Leuthner, *ibid.*, 1939, **241**, 57 ($MgO + TiO_2$); W. Jander and K. Grob, *ibid.*, 1940, **245**, 67 ($NiO + Al_2O_3$); W. Jander and W. Wenzel, *ibid.*, 1941, **246**, 67 ($CuO + WO_3$); W. Jander and H. Riehl, *ibid.*, p. 81 ($ZnO + SiO_2$); W. Jander and G. Lorenz, *ibid.*, 1941, **248**, 105 ($MgO + V_2O_5$); cf. also G. F. Hüttig and H. Theimer, *ibid.*, 1941, **246**, 51 ($ZnO + Cr_2O_3$).

[9] W. Jander (with H. Herrmann), *ibid.*, 1939, **241**, 225.

[10] *Bull. Soc. chim.*, 1941, **8**, 209.

[11] R. Klement and F. Steckenreiter, *Z. anorg. Chem.*, 1940, **245**, 236.

[12] R. Klement and F. Zureda, *ibid.*, 1940, **245**, 229.

[13] See, for example, W. M. Cohn, *Metallwirts.*, 1929, **8**, 367, 599, 623; see also a monograph by W. Fehse, "Elektrische Öfen mit Heizkörpern aus Wolfram" (Sammlung Vieweg, Heft 90, 1928), for various types of high-temperature furnaces.

[14] E. Zintl, W. Morawietz, and E. Gastinger, *Z. anorg. Chem.*, 1940, **245**, 8.

[15] E. Zintl [with W. Bräuning, H. L. Grube, W. Krings, and W. Morawietz], *ibid.*, p. 1.

[16] Pp. 71, 75.

A recent application of the aluminothermic process to the preparation of borides of tungsten and molybdenum is reported;[17] the known boride WB_2 and a new compound, $Mo_7Al_6B_7$, have been obtained. The existence of solid compounds of apparently complex composition, such as $Mo_7Al_6B_7$, is an interesting feature of modern work on solids which offers a wide field for further study. An improved method of preparing aluminium boride, AlB_{12}, by the aluminothermic reaction has also been described.[18]

Certain important aspects of reactions between solid materials and gases have been studied recently. In their studies on the reactions of solids, G. F. Hüttig and his collaborators have included investigations on the degassing of solids,[19] and on the effects of foreign gases on solid–solid and gas–solid reactions.[20, 21] The fact that reactions between solid substances may be accelerated or retarded by the presence of gases which do not combine with the reactants is of some practical importance; for example, the reaction of calcium sulphate with silica at 1100° (affording calcium silicate) proceeds best in an atmosphere of water vapour.[21] The "activation" of solids in reactions with gases has been further studied by R. Schenck and his co-workers,[22] who have shown that silver mixed with Mn_2O_3, Cr_2O_3, or Rh_2O_3 combines rapidly with oxygen at 400—800°, a temperature range in which the pure metal does not react with oxygen at normal pressures. The effect of the added oxide is due to formation of a stable compound (of type $Ag_2Mn_2O_4$) having a low dissociation pressure of oxygen. Vanadium sesquioxide activates the silver in a similar manner after oxidation to the pentoxide, but alumina and ferric oxide have no effect.

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[17] F. Halla and W. Thury, *Z. anorg. Chem.*, 1942, **249**, 229.

[18] F. Halla and R. Weil, *Z. Krist.*, 1939, **101**, 435.

[19] G. F. Hüttig, H. Theimer, and W. Breuer, *Z. anorg. Chem.*, 1942, **249**, 134; G. F. Hüttig and W. Bludan, *ibid.*, 1942, **250**, 36.

[20] G. F. Hüttig, E. Herrmann, W. Neugebauer, R. Rudisch, R. Wallouch, and O. Hnevkovsky, *Kolloid-Z.*, 1942, **92**, 9; *Ber. deut. keram. Ges.*, 1940, **21**, 429; K. Sedlatschek, *Z. anorg. Chem.*, 1942, **250**, 23.

[21] F. von Bischoff, *ibid.*, p. 10.

[22] R. Schenck, A. Bathe, H. Keuth, and S. Süss, *ibid.*, 1942, **249**, 88. For earlier papers by R. Schenck *et al.* on this subject, see *ibid.*, 1929, **184**, 39; 1932, **206**, 273; 1934, **220**, 97.

An interesting series of gas-solid reactions in which gaseous oxygen is used as an oxidising agent in presence of sodium oxide has been investigated. Mixtures of sodium iodide and sodium oxide (or the peroxide or hydroxide) react with air or oxygen at 400—700° to form the periodate Na_5IO_6.[23] Similarly, the "mixed oxide" Na_2PrO_3, containing quadrivalent praseodymium, is formed by heating Pr_2O_3 with sodium oxide at 470°, in oxygen,[24] and the orthobismuthate, Na_3BiO_4, is obtained from Bi_2O_3, sodium oxide, and oxygen or air at 650°.[25] In these reactions the alkali oxide appears to have a stabilising effect on the higher valency shown by the element undergoing oxidation; clearly, a number of other compounds of similar types may be readily obtainable by analogous reactions.

Reference has been made previously in these Reports to boron oxyfluoride.[26] It has now been shown [27] that boron trifluoride reacts with alumina at 450° according to the following equation: $Al_2O_3 + 2BF_3 = 2AlF_3 + B_2O_3$; the boron trioxide formed in this primary reaction is volatilised as the oxyfluoride. At higher temperatures the reaction can proceed in the reverse direction. Boron trifluoride also reacts with silica at 450°, affording silicon tetrafluoride and boron oxyfluoride; titanium dioxide reacts similarly, but more slowly, whereas ferric oxide will not react at temperatures below 500°. Analogous reactions occur with compounds such as silicates and aluminosilicates, the electropositive constituents of these remaining as their fluorides or borofluorides. These new reactions may find useful application, for instance in the treatment of silicate minerals.

The study of hydrothermal reactions, involving liquid water at temperatures above 100°, offers interesting possibilities. In three recent papers on this subject,[28] W. Jander and his collaborators have discussed the formation of magnesium hydrosilicates, and investigated the system $CaO-SiO_2-H_2O$. Work in this field may have important applications, apart from its geochemical interest.

No review of technique would be complete without some reference to the methods applied by W. Biltz and his school in their studies on affinity; these continue to give successful results in investigations on metallic phosphides.[29] The general method used is to heat a number of mixtures containing different proportions of the combining elements, and examine the products by *X*-ray powder analysis, density determinations, and degradation in a tensimeter at suitable temperatures. The formation of compounds is indicated by the appearance of new lines in the X-radiograms, and by breaks in the pressure–composition curves given by the tensimetric measurements. These methods have served to clarify the chemistry of many simple binary systems.

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[23] E. Zintl and W. Morawietz, *ibid.*, 1940, **245**, 20. [24] *Idem, ibid.*, p. 26.

[25] E. Zintl and K. Scheiner, *ibid.*, p. 32. [26] *Ann. Reports*, 1940, **37**, 127.

[27] P. Baumgarten and W. Bruns, *Ber.*, 1941, **74**, 1232.

[28] W. Jander and R. Fett, *Z. anorg. Chem.*, 1938, **235**, 273; 1939, **242**, 145; W. Jander and B. Franke, *ibid.*, 1941, **247**, 161.

[29] F. E. Faller, E. F. Strotzer, and W. Biltz, *ibid.*, 1940, **244**, 317 (rhodium phosphides); M. Heimbrecht, M. Zumbusch, and W. Biltz, *ibid.*, 1941, **245**, 391 (uranium phosphides); M. Zumbusch and W. Biltz, *ibid.*, 1941, **246**, 35 (tantalum phosphides); F. E. Faller and W. Biltz., *ibid.*, 1941, **248**, 209 (tungsten, molybdenum, and chromium phosphides); M. Zumbusch and W. Biltz, *ibid.*, 1942, **249**, 1 (vanadium phosphides); A. Reinecke, F. Wiechmann, M. Zumbusch, and W. Biltz, *ibid.*, p. 14 (niobium phosphides). See also a general article by W. Biltz, *Angew. Chem.*, 1941, **54**, 320.

Another useful method of studying equilibria in systems involving sulphides had been applied by R. Schenck.[30-32] The equilibrium proportions of hydrogen and hydrogen sulphide established in reactions of the type $NiS + H_2 = Ni + H_2S$ are observed, and the composition of stable solid phases is deduced from breaks in the isotherms obtained by plotting the equilibrium percentage of hydrogen sulphide against the composition of the solid mixture. In the system Ni–Sb–S this method has shown the existence of the compounds NiS, Ni_6S_5, Ni_3S_2, NiSbS, NiSb, and $NiSb_2$;[31] in the corresponding system with cobalt the compounds are CoS, Co_3S_4, Co_9S_8, CoSbS, and $Co_{15}Sb_9S_{17}$.[32]

Methods of thermal analysis applied to binary systems continue to yield useful results. The system magnesium–germanium is shown to give a compound Mg_2Ge, corresponding with similar compounds of magnesium with silicon, tin, and lead.[33] In the system silicon–arsenic two compounds, SiAs and $SiAs_2$, occur as stable solid phases.[34] Special interest attaches to the application of thermal analysis at temperatures in the range $-70°$ to $-145°$, by which the existence of a compound BF_3,SO_2 has been demonstrated;[35] additive compounds of boron trifluoride with hydrogen chloride, methyl chloride, or nitrous oxide could not be detected.

An interesting contribution to the study of molten mixtures at high temperatures is the introduction of coloured indicators to show changes in oxygen-ion activity in oxysalt melts.[36] The colour change due to oxidation of tervalent chromium to the sexavalent state may be used for this purpose. The method has recently been applied to melts containing sodium oxide, boron trioxide, and one of several acidic or basic oxides, with the chromium indicator.[37] The proportions of sodium oxide and boron trioxide required to give a neutral tint to the indicator in the absence of added oxide are first determined; the third oxide is then added, and the new proportion of sodium oxide to boron trioxide required to maintain " neutrality " is found. The result is a measure of the acidity or basicity of the added oxide.

Little attention has been given here to vacuum manipulation of volatile substances, largely because recent issues of these Reports have mentioned a very large number of applications of vacuum technique. Reference must

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[30] R. Schenck, I. Hoffmann, W. Knepper, and H. Vögler, *Z. anorg. Chem.*, 1939, **240**, 173.

[31] R. Schenck and P. von der Forst, *ibid.*, 1939, **241**, 145.

[32] *Idem, ibid.*, 1942, **249**, 76.

[33] W. Klemm and H. Westlinning, *ibid.*, 1941, **245**, 365.

[34] W. Klemm and P. Pirscher, *ibid.*, 1941, **247**, 211.

[35] H. S. Booth and D. R. Martin, *J. Amer. Chem. Soc.*, 1942, **64**, 2198.

[36] W. Stegmaier and A. Dietzel, *Glastech. Ber.*, 1940, **18**, 297, 353.

[37] H. Lux and E. Rogler, *Z. anorg. Chem.*, 1942, **250**, 159.

be made, however, to the special methods required for the manipulation of fluorine and its volatile derivatives; these have been discussed in a recent Tilden lecture[38] and a review on the preparation of fluorine.[39] Continued interest in fluorine chemistry is shown by a recent paper on chromium fluorides.[40] If fluorine is passed over chromium, chromic chloride, or chromic fluoride at 350—500°, the tetra- and penta-fluorides are formed. The former is a brown solid which volatilises perceptibly at 150°, and the latter is a brilliant red compound which is liquid at 100°. At temperatures below 100° a small quantity of hexafluoride is obtained. Chromyl fluoride, CrO_2F_2, is obtained as a brown gas, condensing to brownish-red crystals with a vapour pressure of 24 mm. at 0°, by treating chromyl chloride with fluorine at 200°. The chromyl fluoride changes readily into a light-coloured polymeride melting at about 200°.

Interest continues in reactions in non-aqueous solvents. A useful description has recently been given of the apparatus and methods used to prepare cobalt and chromium amides by reactions between potassium amide and the cobalt or chromium hexammine nitrate in liquid ammonia solution.[41] Methods of carrying out certain reactions of the products are also described. A compound of univalent nickel, $K_2Ni(CN)_3$,[42] has recently been isolated as a red solid by the action of sodium or potassium (or calcium [43]) on excess of $K_2Ni(CN)_4$ in liquid ammonia solution.[44] If excess of alkali metal or calcium is used in this reaction the product is not $K_2Ni(CN)_3$, but $K_4Ni(CN)_4$, a copper-coloured solid which is oxidised on momentary exposure to air. Other complex cyanides [$K_2Cd(CN)_4$, $K_3Cu(CN)_4$, $KAg(CN)_2$, and $K_2Zn(CN)_4$] give the free heavy metals on reduction with potassium or sodium in liquid ammonia; the products (except zinc) are pyrophoric.[43] Pure $NaNbF_6$ and Na_2NbF_7 have recently been prepared by crystallisation of solutions of the component fluorides (NaF and NbF_5) in anhydrous liquid hydrogen fluoride.[45] The use of this solvent has obviated difficulties due to hydrolysis of the fluorides in aqueous media.

The use of magnetic susceptibility measurements in the study of molecular constitution is now well established.[46] In the past there has been some speculation regarding the constitution of the so-called " even " polyhalides, such as CsI_4. It has now been found that CsI_4 is diamagnetic, showing that its molecule contains no unpaired electrons;[47] the simple formula CsI_4

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[38] H. J. Emeléus, *J.*, 1942, 441.

[39] G. H. Cady, D. A. Rogers, and C. A. Carlson, *Ind. Eng. Chem.*, 1942, **34**, 443.

[40] H. von Wartenberg, *Z. anorg. Chem.*, 1941, **247**, 135.

[41] O. Schmitz-Dumont, J. Pilzecker, and H. F. Piepenbrink, *ibid.*, 1941, **248**, 175. See also p. 77 of this Report.

[42] See I. Bellucci and R. M. Corelli, *Z. anorg. Chem.*, 1914, **86**, 88.

[43] J. W. Eastes and W. M. Burgess, *J. Amer. Chem. Soc.*, 1942, **64**, 2715.

[44] *Idem, ibid.*, p. 1187.

[45] A. W. Laubengayer and C. G. Polzer, *ibid.*, 1941, **63**, 3264.

[46] See W. Klemm, " Magnetochemie " (Physik und Chemie und ihre Anwendungen in Einzeldarstellungen, Vol. I), Leipzig, 1936; S. S. Bhatnagar and K. N. Mathur, " Physical Principles and Applications of Magnetochemistry," London, 1935.

[47] S. S. Hubard, *J. Physical Chem.*, 1942, **46**, 227.

requires one unpaired electron in the molecule, and the simplest formula permitted by the magnetic data is Cs_2I_8. The constitution $Cs[I_3-I_2-I_3]Cs$, in which an iodine molecule is " shared " between two tri-iodide groups, is suggested. It now remains for the structure to be determined by *X*-ray methods. The magnetic behaviour of a number of metallic complexes of salicylaldehyde imines has recently been examined.[48] These complexes, many of which contain quadridentate groups, afford interesting examples of different types of bonding between the metal atoms and the organic groups, the magnetic data giving important information on these bond types. The more rigorous application of magnetic measurements and *X*-ray data in determining the constitution of solids is typified by an investigation on the dihalides of titanium and vanadium.[49]

The usefulness of electron-diffraction observations in establishing the nature of surfaces is shown by recent work on the surface reaction of zinc oxide with hydrogen selenide.[50] This reaction ceases when the product contains about 6% of selenium. *X*-Ray examination indicates that it consists chiefly of unreacted zinc oxide, but in electron-diffraction photographs the pattern due to zinc selenide largely predominates. It is deduced that the selenide forms a coherent coating on the oxide particles, the electron-diffraction method showing the structure of the surface rather than that of the interior of the particles.

A new experimental tool with potential applications in Inorganic Chemistry is the electron microscope. The colloidal nature of molybdenum-blue (shown to have the formula Mo_8O_{23},nH_2O) is strikingly demonstrated by an electron photomicrogram giving a magnification of 62,000 diameters;[51] the particle size is found to be of the order of 100 A.

In conclusion, reference may be made to a recently published book dealing at some length with reactions in electric discharges,[52] a subject which merits continued interest; recent new applications of electric discharge techniques appear to be lacking. A. J. E. W.

H. J. Emeléus.
A. L. G. Rees.
A. J. E. Welch.

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[48] W. Klemm and K. H. Raddatz, *Z. anorg. Chem.*, 1942, **250**, 207.

[49] W. Klemm and L. Grimm, *ibid.*, 1942, **249**, 198, 209.

[50] M. L. Fuller and C. W. Siller, *J. Appl. Physics*, 1941, **12**, 416.

[51] F. B. Schirmer, jun., L. F. Audrieth, S. T. Gross, D. S. McClellan, and L. J. Seppi, *J. Amer. Chem. Soc.*, 1942, **64**, 2543.

[52] G. Glockler and S. C. Lind, " The Electrochemistry of Gases and other Dielectrics," New York, 1939.

CRYSTALLOGRAPHY.

1. INTRODUCTION.

THE more physical sections of last year's Report dealt with the diffuse X-ray reflections from crystals, and with metal structures. Although a very large number of new papers on these subjects have appeared during the year, they are not further reviewed in the present Report. It is difficult to deal adequately with the whole subject of modern X-ray crystallography each year, and improvements in the technique of analysis have not been mentioned for some time. Hence a short section is now devoted to this subject. Since this was last reviewed [1] the use of intensity data and Fourier series methods has become more common in crystal analysis, and a number of improvements and suggested modifications in technique have been made. One of the most interesting developments is that of the "X-Ray Microscope" by Sir W. L. Bragg, which provides a direct optical method for performing Fourier syntheses and giving projections of crystal structures.

In the field of inorganic chemistry a number of interesting structures have been worked out in detail, including those of phosphorus pentachloride, which contains not PCl_5 molecules but a mixture of PCl_4^+ and PCl_6^- ions; and the hydrazinium ion, of interest because of the like formal changes on adjacent atoms. The complex fluorides have been further examined and provide more examples of 6- and 7-co-ordination complexes. The structure of hydrogen peroxide has been determined in an interesting manner, by a quantitative study of its addition compound with urea. The structure is neither *cis-* nor *trans-*, but the more stable intermediate form predicted some time ago by quantum-mechanical calculation.

Carbon compounds have received a lot of attention this year, and a new intermediate structure, in addition to diamond and graphite, has been proposed for the element itself.

dl-Alanine and melamine (cyanuric triamide) are two new structures which have been very carefully determined, and both the inter- and the intra-molecular bond lengths are interesting. The structures of gutta-percha, rubber, and polychloroprene have received considerable attention, but no degree of finality can be attached to these results. In connection with the rubber problem, however, the full and accurate determination of the structure of β-isoprenesulphone is of considerable interest.

In protein structures, some interesting work on hæmoglobin has appeared, careful comparative studies having been made on the crystals in different states of hydration. Some tentative conclusions have been reached regarding the dimensions and orientation of the molecule.

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[1] *Ann. Reports*, 1938, **35**, 174.

2. TECHNIQUE OF STRUCTURE ANALYSIS.

As the trend of crystal analysis passes to the examination of more complex structures, and to the more accurate determination of atomic positions in simple structures, it is inevitable that more and more attention should be paid to intensity data and their interpretation by Fourier series methods. In most of the investigations now being made, the X-ray intensities are obtained by visual estimate from photographic records. If this is done carefully and systematically a surprising degree of accuracy can be reached, sufficient indeed to determine the atomic positions to within very narrow limits in most structures. This has been tested in an interesting manner in a recent analysis [1] carried out independently by two workers, starting from the same X-ray films. They finally obtained almost identical values for the parameters of the structure.

Unless adequate correction can be made for various factors, including absorption (one of the major sources of error), it may be a waste of time to employ elaborate means of intensity measurement. However, if the object of the work is to detect delicate variations in bond lengths rather than mere structural types, then quantitative intensity measurements are required. A number of integrating photometers have been specially designed for crystal analysis and these have been reviewed in a recent article.[2] Where the highest accuracy is not necessary, the more rapid method described by R. H. V. M. Dawton [3] may be employed, which makes use of positive prints from the X-ray negative. Another process, also employing prints, has been mentioned by J. S. Lukesh.[4] A method, which is chiefly of use in correlating very strong and very weak reflections (the range covered may be several thousand to one) consists of the simple device of exposing a number of X-ray films simultaneously in series.[5] Each successive film cuts down the intensity by a factor which is very constant from one film to another, and also constant over the surface of each film. This multiple film technique has been much used in the structure analyses reviewed in Sections 3 and 4.

The principles involved in the construction of powder cameras and their calibration have been described in two recent articles,[6] and a new multiple exposure instrument for making accurate comparisons of spacings has been constructed by A. R. Ubbelohde.[7] E. Orowan [8] has described an ingenious method which gives directly on a stationary film the angular position of the reflecting plane, in rotation or oscillation photographs. A fine grid of parallel wires is placed in front of the film and rotated in its own plane in time with the crystal during the exposure. The wires cast a shadow on each spot and their inclination gives the precise angular setting of the crystal at the time when the reflection takes place—a result which can otherwise only be attained on a much more complicated moving-film instrument.

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[1] See ref. (20), Section 3.

[2] J. M. Robertson, *J. Sci. Instr.*, 1941, **18**, 126.

[3] *Proc. Physical Soc.*, 1938, **50**, 919.

[4] *J. Chem. Physics*, 1941, **9**, 659.

[5] J. J. de Lange, J. M. Robertson, and (Miss) I. Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398, 404.

[6] A. J. Bradley, H. Lipson, and N. J. Petch, *J. Sci. Instr.*, 1941, **18**, 216; A. J. C. Wilson and H. Lipson, *Proc. Physical Soc.*, 1941, **53**, 245.

[7] *J. Sci. Instr.*, 1939, **16**, 155.

[8] *Nature*, 1942, **149**, 355.

For the summation of Fourier series, it seems likely that accurate numerical methods will always be necessary for a final expression of the results; but the Fourier series method is being employed more and more as one of successive approximation, and in the earlier calculations, and in the summing of Patterson series, rapid methods are very desirable. In this connection the most interesting development of recent years is Sir W. L. Bragg's " X-Ray Microscope." [9] In this optical method a projection of the structure is obtained by means of a two-dimensional diffraction grating, which may be constructed by drilling holes in a brass plate. Each X-ray reflection from a given zone is represented by a hole of area proportional to the structure amplitude, and the holes are arranged in the positions of the points in the corresponding section through the reciprocal lattice. With a monochromatic point source of light and appropriate lens system the diffraction caused by the holes results in a very realistic image of the crystal structure being formed as shown in Fig. 1. The positions of the atoms in this structure are shown by black dots in Fig. 2. It is difficult

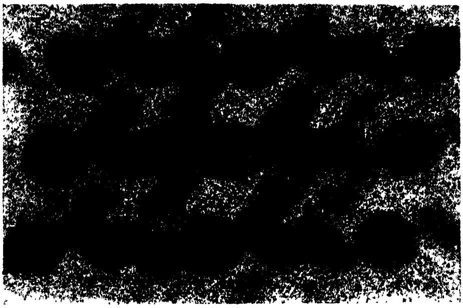

FIG. 1.
Interference Pattern (Diopside).

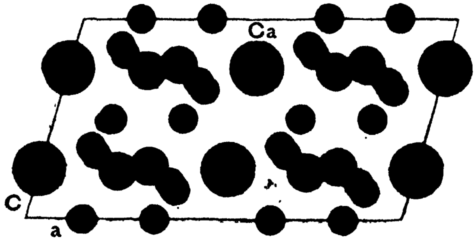

FIG. 2.
Structure of Diopside, $CaMg(SiO_3)_2$, *Projected on* (010).

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[9] *Nature*, 1939, **143**, 678; 1942, **149**, 470; see also H. Boersch, *Z. tech. Physik*, 1938, 337, and M. J. Buerger, *Proc. Nat. Acad. Sci.*, 1939, **25**, 383; 1941, **27**, 117.

to construct a small-scale brass plate with the accuracy necessary for a complicated structure, but it has now been found possible to employ a photographic method, whereby a large drawing of the reciprocal lattice, representing the cross-grating spectra, can be photographed on a much reduced scale on a special type of plate. Optically true glass plates of course are necessary, as the paths of the wave from the various transparent holes must be correct to a fraction of a wave-length. The cross grating for Fig. 1 was produced photographically. The method has definite possibilities as a quick routine way of effecting Fourier summations, particularly when dealing with Patterson series where the amplitudes are always positive.

Sir W. L. Bragg's earlier photographic method of Fourier synthesis,[10] whereby successive exposures were made on a single film or paper of each individual term in the double Fourier series, has now been further developed and made faster and more automatic by M. L. Huggins [11] by means of a set of standard "*hk* masks," one for each term, and the use of special film emulsions which reduce the high background intensity.

A machine for the rapid numerical summation of Fourier series, constructed from simple parts, has been described by D. Macewan and C. A. Beevers.[12] The information contained in the well-known Beevers–Lipson strips is actually built into this machine, so that no selection and sorting of cards or strips is needed. The operation of the machine is very speedy, Fourier terms being added in at the rate of about one every two seconds and the results recorded on a set of sixteen counters.

With regard to mathematical methods, a new type of synthesis of X-ray data has recently been suggested by S. H. Yu.[13] Full details have not been given, but this method appears to be a modified form of the Patterson function, in which less interference of the peaks (better resolution), combined with reduced diffraction effects, is claimed. It has been pointed out,[14] however, that all the advantages claimed cannot be obtained from the X-ray data given by any actual crystal. There is a natural physical limit to the resolving power inherent in the finite size and thermal motion of atoms which compose the crystal.

The application of a least-squares method to refining the trial parameters in a structure determination has been described briefly by E. W. Hughes.[15] It is claimed that this method has several advantages over the Fourier series method; *e.g.*, all the observed structure factors need not be included in every case. Further details will be of interest.

The application of differential radial distribution curves to the analyses of glasses of related compositions has been described by J. S. Lukesh,[16] and the idea of such difference diagrams has been applied to crystal analysis by M. J. Buerger.[17] The simplest case is that of isomorphous centro-

[10] *Z. Krist.*, 1929, **70**, 475.

[11] *J. Amer. Chem. Soc.*, 1941, **63**, 66.

[12] *J. Sci. Instr.*, 1942, **19**, 150.

[13] *Nature*, 1942, **149**, 638.

[14] H. Lipson, *ibid.*, 1942, **150**, 25; C. S. Lu, *ibid.*, p. 407.

[15] *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[16] *Proc. Nat. Acad. Sci.*, 1942, **28**, 277.

[17] *Ibid.*, p. 281.

symmetrical structures with different atoms on the symmetry centre. In this case the difference diagram applied to the Patterson projections gives an undistorted picture of the actual crystal structure. This result, however, can be expressed physically in another way, and has been used, for example, to elucidate the structures of the phthalocyanines.[18] The more general treatment of the method may have interesting applications to solid solutions.

3. INORGANIC STRUCTURES.

There is less than the usual volume of work on inorganic structures to report this year, although a number of accurate determinations of considerable interest have been carried out. Mention of partial or incomplete determinations and work on complex systems and minerals has been largely omitted on account of restrictions on space.

With regard to elements, an important event is the proposal of a new structure for carbon,[1] in addition to the two well-known crystalline varieties, diamond and graphite. A third variety is now necessary in order to explain the appearance of certain extra diffraction lines which are given occasionally by certain specimens of graphite [2] and do not appear to be due to impurities [3] or to diffuse scattering effects.[4] In the new structure there are thought to be three differently disposed layers of carbon atoms in sequence, instead of two as in graphite, before identical repetition is reached. As a result the *c* axis is $1\frac{1}{2}$ times as long as in normal graphite. The structure is described crystallographically as $R\bar{3}m$ with $a = 3{\cdot}635$ A., $\alpha = 39{\cdot}49°$, and atoms at $\pm\ (\frac{1}{6}, \frac{1}{6}, \frac{1}{6})$. It appears to be one possible intermediate structure between diamond and graphite, although not apparently existing as separate single crystals.

A discrepancy found in the carbon–carbon distance for the small graphite crystallites which are formed during the carbonisation of cellulose, coal, etc.,[5] has now been cleared up. These results led to certain carbon–carbon distances as small as 1·37 A. for the carbon rings in microcrystalline graphite as against a value of 1·415 A. in normal macrocrystalline graphite, a result difficult to understand in view of the strong bonding in these net planes. A. Taylor [6] has now found that a correction should be applied to these results, based on a mathematical treatment of *X*-ray diffraction from random layer lattices developed by B. E. Warren,[7] which shows that the diffraction peaks are displaced from their position in the direction of increasing θ by an amount which depends upon the crystal size. For the minute graphite crystallites mentioned, this correction is important, and its application brings the results accurately into line with the normal carbon–carbon graphite distance of 1·415 A.

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[18] J. M. Robertson, *J.*, 1936, 1195.

[1] H. Lipson and A. R. Stokes, *Nature*, 1942, **149**, 328.

[2] G. I. Finch and H. Wilman, *Proc. Roy. Soc.*, 1936, *A*, **155**, 345.

[3] A. Taylor and D. Laidlaw, *Nature*, 1940, **146**, 130.

[4] (Mrs.) K. Lonsdale, (Miss) I. E. Knaggs, and H. Smith, *ibid.*, p. 332.

[5] H. E. Blayden, H. L. Riley, and A. Taylor, *J.*, 1939, 67.

[6] *Nature*, 1942, **150**, 462.

[7] *Physical Rev.*, 1941, **59**, 693.

X-Ray diffraction experiments on liquid argon[8] and oxygen[9] have been described. In addition to the expected peak at about 1·22 A. in the atomic distribution curve for oxygen, due to diatomic molecules, there is a further fairly strong peak at about 2·2 A., probably due to ozone, and third and fourth peaks indicating aggregates of O_2 molecules, or possibly O_4.

Oxides of platinum are difficult to prepare, but one such compound, formed on a platinum wire in use over a period of years, has now been analysed by *X*-ray methods[10] and shown to consist of Pt_3O_4 molecules. The cubic structure ($a = 6{\cdot}226$ A., containing two molecules of Pt_3O_4) has been analysed by Debye–Scherrer photographs and Fourier analysis, which give a Pt–O distance of 2·2 A., and a Pt–Pt approach of 3·113 A.

Silver arsenate[11] has a structure similar to that of silver phosphate, consisting of a cubic body-centred arrangement of arsenic atoms, each surrounded tetrahedrally by oxygen atoms, silver occupying positions on the faces of the unit cube. Interatomic distances are As–O $= 1{\cdot}75 \pm 0{\cdot}05$ A., Ag–O $= 2{\cdot}34 \pm 0{\cdot}05$ A. Potassium dihydrogen arsenate[11] is tetragonal and similar to the corresponding phosphate. In this case the arsenate group is a slightly deformed tetrahedron with O–As–O angles of 104° and 113°. The significant distances are As–O $= 1{\cdot}74 \pm 0{\cdot}03$ A. and O–H . . . O $= 2{\cdot}54 \pm 0{\cdot}03$ A., the latter figure indicating a strong hydrogen bridge similar to that occurring in potassium dihydrogen phosphate. The influence of randomness in the dihydrogen arsenate structure is discussed.

The nature of the hydrogen bridges in acid phosphates has been further studied by A. R. Ubbelohde and (Miss) I. Woodward[12] by means of the isotope effect. The expansion of the lattice which takes place on substituting deuterium for hydrogen in $(NH_4)H_2PO_4$ is in the direction of the hydrogen bridges and of the same magnitude as in the isomorphous KH_2PO_4, but the contraction at right angles is considerably larger in $(NH_4)H_2PO_4$ than in KH_2PO_4. These isotope expansions for the acid phosphates are considerable and can be determined with an accuracy of about ± 2%, but are not so large as those originally noted in oxalic acid dihydrate.[13]

The positions of the lead and chromium atoms in the monoclinic crystals of lead chromate (crocoite)[14] have been determined, but not those of the oxygen atoms, and so the exact structure is still in doubt. The complex structure of tricalcium aluminate $Ca_3Al_2O_6$[15] with 24 molecules in the cubic cell is similarly in doubt with regard to the arrangement of the oxygen atoms. Details have been given of the tetragonal lattice constants and atomic positions in the disilicides of thorium,[16] niobium, tantalum, vanadium, and rhenium.[17]

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[8] A. Eisenstein and N. S. Gingrich, *Physical Rev.*, 1942, **62**, 261.

[9] P. C. Sharrah and N. S. Gingrich, *J. Chem. Physics*, 1942, **10**, 504.

[10] E. G. Galloni and A. E. Roffo, *ibid.*, 1941, **9**, 875.

[11] L. Helmholz and R. Levine, *J. Amer. Chem. Soc.*, 1942, **64**, 354.

[12] *Proc. Roy. Soc.*, 1942, *A*, **179**, 399.

[13] J. M. Robertson and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1939, *A*, **170**, 222.

[14] S. B. Brody, *J. Chem. Physics*, 1942, **10**, 650.

[15] H. F. McMurdie, *J. Res. Nat. Bur. Stand.*, 1941, **27**, 499.

The structure of calcium cyanamide [18] is now reported to be analogous to that of sodium azide, NaN_3, with C–N = 1·16 ± 0·08 A. and Ca–N = 2·49 ± 0·04 A.

A large number of heavy-metal iron cyanides, including Prussian blue and Turnbull's blue, have been studied by means of *X*-ray diffraction patterns obtained from the various iron cyanide gels.[19] It is concluded that they form an isomorphous series of compounds possessing face-centred cubic symmetry, and atomic positions have been proposed.

Fig. 1 gives a general view of the unit cell in the phosphorus pentachloride structure, details of which have now been published by D. Clark, H. M. Powell, and A. F. Wells.[20] The analysis has been carried out with considerable accuracy, from visually estimated intensities, by two independent investigators, and the close concordance of their results is very encouraging. All structures involving discrete PCl_5 molecules, or shared polyhedra, have been eliminated, and it is found that the tetragonal unit cell contains separate tetrahedral PCl_4^+ and octahedral PCl_6^- groups, arranged as shown in Fig. 1. (This result is in keeping with the physical properties of the solid, which suggest an ionised form.) There is an appreciable difference in the P–Cl distances in these two groups, the results averaging 2·06 A. in PCl_6^- and 1·98 A. in PCl_4^+. This difference is in accord with the change in electrical charge.[21]

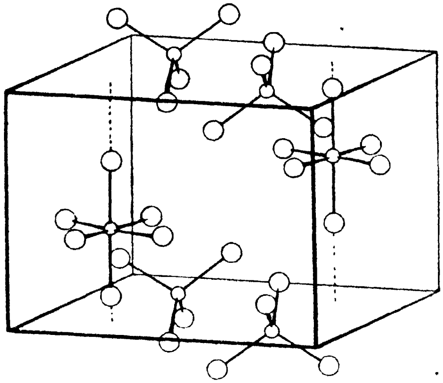

FIG. 1.

General View of Unit Cell. (Small circles, phosphorus ; large circles, chlorine.)

A rather interesting structure has now been proposed for the intermediate-temperature modification of $Ni(NO_3)_2,6NH_3$ by S. H. Yu.[22] It is cubic and consists of flat triangular NO_3 and octahedral $Ni(NH_3)_6$ groups interlocking into a calcium fluoride type of structure. The crystal appears to be neither a single crystal in the usual sense nor a polycrystalline mass, but is what the author terms a double crystal aggregate. Apparently the NO_3 group can assume either one of two alternative configurations which correspond to extreme positions of the oscillating NO_3 groups of the room-temperature modification.

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[16] G. Brauer and A. Mitius, *Z. anorg. Chem.*, 1942, **249**, 325.

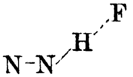
[17] H. J. Wallbaum, *Z. Metallk.*, 1941, **33**, 378.

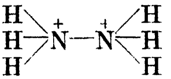
[18] M. A. Bredig, *J. Amer. Chem. Soc.*, 1942, **64**, 1730.

[19] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Physical Chem.*, 1942, **46**, 99.

[20] *J.*, 1942, 642.

[21] L. Pauling and J. Sherman, *Z. Krist.*, 1932, **81**, 1.

Hydrazinium difluoride (I) is of interest as one of those rare stable substances where the structure assigned to the ion places like formal charges on adjacent atoms. The crystal structure has now been fully determined.[23] The rhombohedral cell, space group $R\bar{3}m$, contains one molecule. The layer type of structure resembles that of cadmium chloride. Each hydrazinium ion forms six hydrogen bridges to fluoride ions at the corners of an octahedron elongated in the direction of the N–N axis, the hydrogen atoms in the ion thus having the *trans-* or staggered configuration. Each fluoride ion in turn forms three hydrogen bridges to different $N_2H_6^{++}$ ions. The structure as a whole is a very open one, obviously due to the strongly directed nature of the hydrogen bridges. Their length, N–H . . . F = 2·62 ± 0·02 A., is the shortest yet found between nitrogen and fluorine. The N–N distance is 1·42 A. and the angle  $N{-}N{-}H\cdots F$ is 110°. Ionic structures, of the type (II), (III), (IV), etc., are thought to contribute to the extent of about 75% to the normal state.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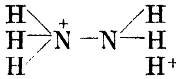
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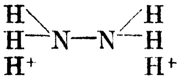
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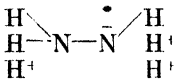
(IV.)

Complex Fluorides.—The structures of the complex fluorides have received considerable attention in recent years.[24] Two distinct types of 7-co-ordination complex are now established. First, there is the distorted octahedron, where the seventh atom is accommodated by spreading one of the faces and inserting the extra atom at its centre, as in the $[ZrF_7]^{\equiv}$ complex.[25] The oxyhexafluoniobate ion $[NbOF_6]^{\equiv}$ is now shown[26] to have essentially this structure, the oxygen being inserted along a three-fold axis on one of the faces, accompanied by some distortion. The symmetry displayed is cubic holohedral, but the data for these structures are incompatible with space-group theory and it is necessary to assume that they are statistical results for structures which display some randomness in the atomic arrangement. The second type of 7-co-ordination complex is that of the $[NbF_7]^=$ and $[TaF_7]^=$ structures,[27] which are based on the trigonal prism with the seventh atom at the centre of one square face, followed by certain distortions.

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[22] *Nature*, 1942, **150**, 347.

[23] M. L. Kromberg and D. Harker, *J. Chem. Physics*, 1942, **10**, 309.

[24] See *Ann. Reports*, 1939, **36**, 170; 1940, **37**, 184; 1941, **38**, 104.

[25] G. C. Hampson and L. Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 2702.

[26] M. B. Williams and J. L. Hoard, *ibid.*, 1942, **64**, 1139.

The latest structure in this series to be examined by J. L. Hoard and M. B. Williams[28] is that of $(NH_4)_3SiF_7$, which forms crystals of tetragonal symmetry (D_{4h}^5–$P4/mbm$). However, all possible structures containing 7-co-ordination complexes, $[SiF_7]^{\equiv}$, have been eliminated by the *X*-ray data, and instead, the structure is shown to be an ordered aggregate of ammonium, octahedral hexafluosilicate, and " extra " fluoride ions, and the compound should be described as ammonium hexafluosilicate–ammonium fluoride, $(NH_4)_2SiF_6,NH_4F$. In the structure, each ammonium ion is near eight fluorine atoms of neighbouring $[SiF_6]^=$ groups and two fluoride ions. The Si–F distance is 1·71 A., F–F = 2·42 A., and the N–F separations vary from 2·8 to 3·1 A. A Fourier projection on the (001) plane is given, along the two-fold axis of the octahedral $[SiF_6]^=$ ion (crystallographic *c* axis). In all these analyses the *X*-ray work has been carried out with care, employing oscillation, Laue, and powder photographs with Cu-$K\alpha$ radiation, and visual estimates of intensities.

Rubidium hexafluogermanate, Rb_2GeF_6, has been re-examined by W. B. Vincent and J. L. Hoard[29] and is now shown to be fully isomorphous with the corresponding ammonium and potassium salts.[30] It consists of an aggregate of K^+ and almost regular octahedral $[GeF_6]^=$ ions. The dimensions are almost identical with those of the ammonium salt, the effective radii of rubidium and ammonium ions being about the same, except when the ammonium ion is restricted to a small co-ordination number (4) by the formation of strong hydrogen bonds.

Structure of Hydrogen Peroxide.—The direct crystal analysis of hydrogen peroxide is a matter of considerable experimental difficulty, and hence the very complete analysis of its addition compound with urea [" hyperol," $CO(NH_2)_2,H_2O_2$] now made by C. S. Lu, E. W. Hughes, and P. A. Giguère[31] is of interest. The structure of urea is already accurately known.[32] The addition product has been analysed, moving-film methods and estimation of intensities by the multiple film technique[33] being employed. The orthorhombic crystal, $a = 6{\cdot}86$, $b = 4{\cdot}83$, $c = 12{\cdot}92$ A., D_{2h}^{14}–*Pnca*, contains 4 molecules of $CO(NH_2)_2,H_2O_2$, and all the parameters have been determined and refined by Fourier series methods. It is found that each nitrogen atom of urea makes two hydrogen bridges of 3·04 and 2·94 A. to peroxide oxygens of two different peroxide molecules, and that the carbonyl oxygen of urea makes two very strong hydrogen bridges (2·63 A.) to other peroxide molecules, as indicated diagrammatically in (V) and (VI). The urea molecule is found to have the same configuration as in the urea crystal.[32] The hydrogen atoms of hydrogen peroxide being assumed to lie along the strong hydrogen bonds directed towards the carbonyl oxygens, the structure shown in Fig. 2 is obtained for hydrogen peroxide. This structure is in very good agreement with that predicted in 1934 by W. G. Penney and G. B. B. M. Sutherland [34] for this molecule by a quantum-mechanical calculation by the method of electron pairs. They found that a model of this type, with the H–O–O angle and the dihedral angle both about 100°, was more stable than either the *cis*- or the *trans*-configuration. The structure is also in agreement with dipole-moment determinations.[35] The O–O distance obtained in the present investigation is 1·46 ± 0·03 A., and this is in agreement with electron-diffraction determinations.[36]

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[27] J. L. Hoard, *J. Amer. Chem. Soc.*, 1939, **61,** 1252.

[28] J. L. Hoard and M. B. Williams, *ibid.*, 1942, **64,** 633.

[29] *Ibid.*, p. 1233.

[30] J. L. Hoard and W. B. Vincent, *ibid.*, 1939, **61,** 2849.

[31] *Ibid.*, 1941, **63,** 1507.

[32] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, 1930, **75,** 529; 1934, **89,** 462.

[33] J. J. de Lange, J. M. Robertson, and (Miss) I. Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171,** 398.

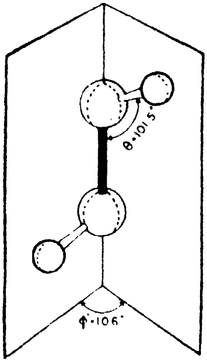
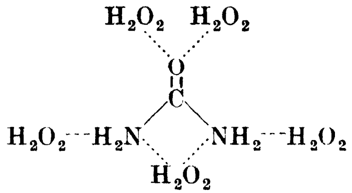
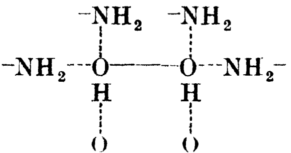


FIG. 2.

A perspective view of the hydrogen peroxide molecule. The hydrogen atoms (represented by smaller spheres) are assumed to lie along hydrogen bonds, and the length of the O–H *bonds is taken as* 0·96 A.



(V.)



(VI.)

4. ORGANIC STRUCTURES.

Quite a large number of quantitative studies of organic crystals and molecules have been made during the year. Electron-diffraction studies have given interesting results on methylene*cyclo*butane.[1] There are no unusual bond distances to report, but this is the first four-membered carbon ring compound to be measured, and it is found that the carbon atoms are coplanar, lying at the corners of a square, with 90° bond angles. The fifth carbon atom, attached by a double bond, lies on the extension of one of the diagonals. The bond lengths are normal, within the limits of experimental error (± 0·03 A.). In hexamethylethane [1] the central C–C bond appears to be somewhat stretched (1·58 ± 0·03 A.) but the other distances are normal. The experimental results in this case are scarcely capable of distinguishing between models involving free rotation, eclipsed or staggered configurations for the methyl groups, but the observations favour the latter slightly.

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[34] *Trans. Faraday Soc.*, 1934, **30**, 898; *J. Chem. Physics*, 1934, **2**, 492.

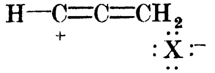
[35] E. P. Linton and O. Maass, *Canadian J. Res.*, 1932, **7**, 81.

[36] P. A. Giguère and V. Schomaker, unpublished preliminary results.

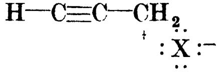
[1] S. H. Bauer and J. Y. Beach, *J. Amer. Chem. Soc.*, 1942, **64**, 1142.

In view of the interesting carbon–carbon distances found in methylacetylene,[2] the propargyl halides have now been examined,[3] and the carbon–carbon single bond is again found to have the value 1·47 ± 0·02 A., as in methylacetylene. The carbon–halogen distances are somewhat larger than normal, being 1·83, 1·95, and 2·13 A., for C–Cl, C–Br, and C–I instead of 1·76, 1·91, and 2·10 A., as calculated from the covalent radii. It is thought that this is possibly due to contributions from the extra ionic structure (I) in addition to the usual ionic structure (II).

(I.)



$$\begin{array}{l}\mathrm{H{-}C{=}C{=}CH_2}\\ \qquad\;\, {}^{+}\qquad\;\; :\underset{..}{\ddot{\mathrm{X}}}:^{-}\end{array}$$



$$\begin{array}{l}\mathrm{H{-}C{\equiv}C{-}CH_2}\\ \qquad\qquad\quad {}^{+}\; :\underset{..}{\ddot{\mathrm{X}}}:^{-}\end{array}$$

(II.)

(Miss) I. E. Knaggs and (Mrs.) K. Lonsdale[4] have begun an *X*-ray investigation of the esters of the interesting series of polyenedicarboxylic acids of general formula $CO_2H{\cdot}[CH{:}CH]_n{\cdot}CO_2H$. Data are given for the first two members, *trans-trans*-methyl fumarate, $C_6H_8O_4$, and *trans-trans*-methyl muconate, $C_8H_{10}O_4$. The two crystals are structurally similar and belong to the triclinic pinacoidal class with one centrosymmetrical molecule per unit cell (space group $P\bar{1}$). *X*-Ray intensity data, " diffuse spot " phenomena, and magnetic properties combine to show that the chain-like molecules are nearly, if not quite, planar, and lie approximately in the (100) crystal plane. The structures are obviously suitable for detailed analyses, which should yield results of interest.

Preliminary data have also been given for the crystal structure of biotin,[5] where there are four asymmetric molecules of $C_{10}H_{16}O_3N_2S$ in an orthorhombic unit cell, with $a = 5{\cdot}25$, $b = 10{\cdot}35$, $c = 21{\cdot}0$ A., space group $P2_12_12_1$.

dl-*Alanine*.—A very full and accurate account of the structure of *dl*-alanine has now been published by H. A. Levy and R. B. Corey.[6] The orthorhombic cell (C_{2v}^{9}–Pna) contains four asymmetric molecules of $CH_3{\cdot}CH(NH_2){\cdot}CO_2H$, and the difficulty of the analysis is increased by the fact that this complicated three-dimensional structure yields no clear projection in which the positions of the atoms may be resolved by the usual Fourier series methods. Nevertheless, the parameters have been carefully refined, and excellent agreements obtained between the calculated and observed values of the structure factors. The experimental data have been obtained by visual estimation of the intensities, using the Weissenberg camera and multiple-film technique.[7]

[2] See *Ann. Reports*, 1939, **36**, 175.

[3] L. Pauling, W. Gordy, and J. H. Saylor, *J. Amer. Chem. Soc.*, 1942, **64**, 1753.

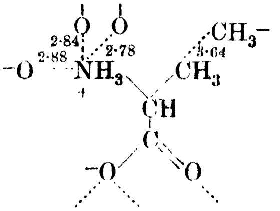
[4] *J.*, 1942, 417.

[5] I. Fankuchen, *J. Amer. Chem. Soc.*, 1942, **64**, 1742.

[6] *Ibid.*, 1941, **63**, 2095.

[7] See ref. (5), Section 2.

It is found that the molecules are linked together by a three-dimensional framework of moderately strong hydrogen bridges (about 2·8 A. in length) and this appears to be responsible for an abnormally close approach (3·64 A.) of the methyl groups of adjacent molecules. The arrangement is shown diagrammatically in (III). The close approach of the methyl groups imposed by the strong intermolecular forces probably prevents these groups from undergoing any rotational motion of the kind thought to exist in other crystals when the methyl–methyl contact distances are larger.[8] One interesting feature of the present work is that probable positions have been assigned to all the hydrogen atoms in the structure and their scattering contributions have been included in the calculation of the structure factors. A small but significant improvement is said to result from this procedure.



(III.)

The alanine molecule has more or less the expected configuration. The α-carbon atom and the carboxyl group are coplanar to within the limits of experimental errors (for interatomic distances about 0·03 A., and for bond angles about 3°). The C–O distances in the carboxyl group are also substantially equal, at 1·23 and 1·25 A., and are in excellent agreement with those proposed for the oxalic acid dihydrate structure.[9] The C–C distances are normal at 1·54 A., but the C–N distance of 1·42 A., although similar to that found in glycine (1·39 A.) and in diketopiperazine [10] (1·41 A.), is much less than the value found for C–N single bonds in most structures, or that computed from the covalent radii.[11] The reason for this contraction is not yet fully understood, but it is one of the significant experimental results which should be considered when attempts are made to arrive at the configuration of polypeptide chains in protein structures.

Melamine (*Cyanuric Triamide*).—A preliminary account of this structure by (Miss) I. E. Knaggs and (Mrs.) K. Lonsdale was mentioned last year,[12] and now a full analysis has been given by E. W. Hughes.[13] The monoclinic unit cell ($P2_1/a$) contains four molecules of $C_3N_6H_6$, and all the parameters have been determined and refined by several Fourier projections. The final result is shown in Fig. 1, which gives the molecular dimensions. The bond lengths are estimated not to be in error by more than 0·05 A., and the molecule is planar. The significant feature is the approximate equality of all the C–N links, which indicate almost complete resonance of the three double bonds about the three carbon atoms, as in (IV)—(VI). The calculated bond length for equal contributions from these structures is 1·343 A., which agrees very closely with the average value found (1·346 A.).

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[8] L. Pauling, *Physical Rev.*, 1930, **36**, 430.

[9] J. M. Robertson, *Trans. Faraday Soc.*, 1940, **36**, 917.

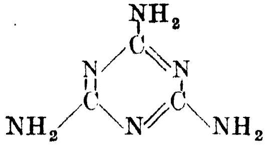
[10] See *Ann. Reports*, 1939, **36**, 179.

[11] V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

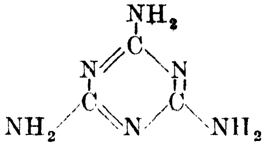
[12] *Ann. Reports*, 1941, **38**, 107.

[13] *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

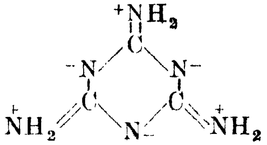
This result is in agreement with the bond lengths about the guanidine carbon atom in dicyanamide,[14] and those of the inner ring system of the



(IV.)



(V.)



(VI.)

phthalocyanine molecule,[15] but in the ring of cyanuric triazide there appear to be alternate long and short bonds of 1·38 and 1·31 A.[16]

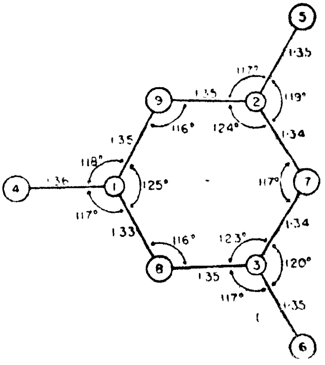


FIG. 1.

The melamine molecule. Small circles, carbons ; large circles, nitrogen ; hydrogens not shown. The molecule is coplanar. Bond lengths are in Ångström units.

The packing of the molecules in the crystal is governed by the formation of hydrogen bridges between the ring nitrogen and the amino-groups of neighbouring molecules. These seem, however, to be of a rather weak type, four pairs of distances varying from 3·00 to 3·10 A. being recorded.

Melamine monohydrochloride hemihydrate is also briefly examined in the same paper.[13] The orthorhombic unit cell contains eight molecules, and there is no obvious resemblance to the melamine structure.

Organic Selenium Compounds.—J. D. McCullough and G. Hamburger have completed accurate studies of diphenylselenium dibromide and dichloride.[17] The compounds are of interest in connection with the effect of the unshared electron pair on the bond orientation and interatomic distances. (In the simpler but similar compounds, tellurium tetrachloride [18] and potassium fluoroiodate,[19] the structures are probably of the trigonal

[14] E. W. Hughes, *J. Amer. Chem. Soc.*, 1940, **62**, 1258; *Ann. Reports*, 1940, **37**, 192.

[15] J. M. Robertson, *J.*, 1936, 1195.

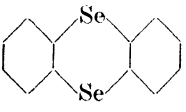
[16] (Miss) I. E. Knaggs, *Proc. Roy. Soc.*, 1935, *A*, **150**, 576.

[17] *J. Amer. Chem. Soc.*, 1941, **63**, 803; 1942, **64**, 508.

[18] D. P. Stevenson and V. Schomaker, *ibid.*, 1940, **62**, 1267.

[19] L. Helmholtz and M. T. Rogers, *ibid.*, p. 1537.

bipyramidal type with the unshared pair in one of the equatorial positions.) The heavy atoms in the diphenylselenium dihalides have simplified the analysis and made it possible to proceed by accurate Patterson and Fourier projections. The molecules are found to have a two-fold axis of symmetry, and to approximate closely to the trigonal bipyramidal structure with selenium at the centre, halogen at the apices, and the equatorial positions occupied by the phenyl groups and the unshared pair. Thus, for the dibromide, Br–Se–Br = 180° ± 3°, C–Se–C = 110° ± 10°, Se–Br = 2·52 ± 0·01 A., Se–C = 1·91 ± 0·03 A. The dichloride is not isomorphous with the dibromide, the orthorhombic unit cell containing eight molecules of $Se(C_6H_5)_2Cl_2$ instead of four in the case of the dibromide, but the molecular structure is essentially the same, with Se–Cl = 2·30 ± 0·05 A. The selenium–halogen distances are thus greater than the sum of the single-bond radii (Calc. : 2·31 for Se–Br and 2·16 for Se–Cl), the lengthening effect being due to the unshared pair.



(VII.)

In selanthren[20] (VII) measurements have now been made, by means of a Fourier projection, of the angle of fold about the line joining the selenium atoms, which give a result of 127°. The C–Se distance is 1·96 A., and the selenium valency angle is about 96°.

Linear Polyesters.—A large number of trimethylene glycol polyesters of high molecular weight have been prepared and their fibre patterns examined by C. S. Fuller, C. J. Frosch, and N. R. Pape;[21] *X*-ray diagrams from both the stretched and the unstretched fibres have been examined, and the patterns obtained depend to some extent on the manner in which the samples are prepared. It is concluded that the chain molecules are essentially of the planar zigzag type, but that the chains are tilted to the fibre axis at an angle of about 30°, rather than being coiled or kinked parallel to this axis. This unexpected result appears to be connected with the layers of ester group dipoles present in the structure. Stretching the fibre causes a decrease in the angle of inclination of the chains to the fibre axis, with a re-orientation of the dipole layers.

Gutta-percha, Rubber, and Polychloroprene.—A series of papers on the molecular structure and properties of these polymers has been published during the year. The crystal-structure determinations are mainly in agreement with earlier work,[22] but C. W. Bunn[23] now gives an exhaustive discussion and investigation of the permissible configurations of the isoprene unit in these structures, and attempts to correlate the results with the physical properties of the substances. The *X*-ray data, obtained by Cu-*Kα* radiation from normal fibre photographs, consist of 24 observed reflections from β-gutta-percha, 40 from rubber, and 18 from polychloroprene; but only about 10 of these reflections can be separately indexed for each structure, the remainder being attributable to small groups of planes of closely similar spacings. Visual estimates of the intensities are given. The structures are described in terms of the following units : β-gutta-percha, $[\text{-CH}_2\text{-C(CH}_3)\text{=CH-CH}_2\text{-}]_n$, orthorhombic, $a = 7{\cdot}78$, $b = 11{\cdot}78$, $c = 4{\cdot}72$ A., space group $P2_12_12_1$ with four long-chain molecules parallel to the c axis; rubber, $[\text{-CH}_2\text{-C(CH}_3)\text{=CH-CH}_2\text{-}]_n$, monoclinic, $a = 12{\cdot}46$, $b = 8{\cdot}89$, $c = 8{\cdot}10$, $\beta = 92°$, space group $P2_1/a$, with four long-chain molecules parallel to the c axis; polychloroprene, $[\text{-CH}_2\text{-CCl=CH-CH}_2\text{-}]_n$, completely analogous to β-gutta-percha, but with $a = 8{\cdot}84$, $b = 10{\cdot}24$, $c = 4{\cdot}79$ A.

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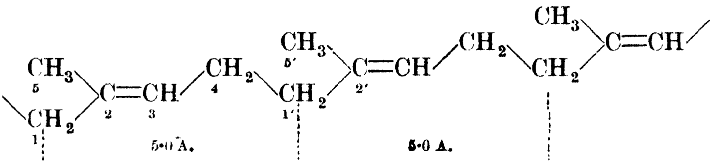
[20] R. G. Wood and G. Williams, *Nature*, 1942, **150**, 321.

[21] *J. Amer. Chem. Soc.*, 1942, **64**, 154. Earlier papers; C. S. Fuller and C. L. Erickson, *ibid.*, 1937, **59**, 344; C. S. Fuller and C. J. Frosch, *ibid.*, 1939, **61**, 2575; *J. Physical Chem.*, 1939, **43**, 323.

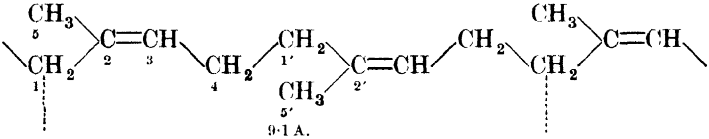
[22] K. H. Meyer and H. Mark, *Ber.*, 1928, **61**, 1939.

[23] *Proc. Roy. Soc.*, 1942, *A*, **180**, 40, 67, 82.

The fundamental difference between gutta-percha and rubber is attributed (in accord with earlier suggestions) to the isomerism which arises from the presence of double bonds in the chains of 1 : 4-isoprene polymers. The *trans*-form (VIII) (with the chain bonds 1, 2, and 3, 4 on opposite sides of the double bond) has a repetition period of 5·0 A., normal interatomic distances and bond angles being assumed, while the *cis*-form (IX) (with chain bonds on the same side of the double bond) has a period of 9·1 A., if



(VIII; *trans*-.)



(IX; *cis*-.)

all the chain carbons lie in a plane. Many different types of chain can be compounded from these isoprene units, but only the *trans*-model can give a one-period unit, of about 5 A., and there appear to be only two types of *cis*-model which give a two-period unit. The possibilities are thus considerably narrowed, and it is generally assumed that β-gutta-percha and chloroprene represent the *trans*-configuration ($c = 4{\cdot}7$ A.) while rubber represents the *cis*-configuration ($c = 8{\cdot}1$ A.). The author discusses the precise form of these chains in considerable detail. In β-gutta-percha the chain carbons of each isoprene unit are thought to lie in a plane, as required by stereochemical considerations. To explain the observed periodicity (4·7 A.) and the X-ray intensities, however, it must be assumed that adjacent isoprenes are not coplanar, bond 1′–4 being moved out of the plane by appropriate rotation around bonds 3–4 and 1′–2′, the isoprene units themselves being kept parallel. In addition, the methyl group (5) is considerably displaced (by 0·65 A.) out of its ideal position in plane 1–2–3–4, the main cause of this being repulsion by the adjoining $-CH_2$ group. In rubber, there are further deviations from the ideal structure, and the two isoprene units which make up an identity period are probably not identical in configuration. [A weak (001) reflection is observed.] There are other distortions, including a certain non-planarity in the isoprene units, which differ from those of the β-gutta-percha structure. The polychloroprene structure is very similar to that of β-gutta-percha, except that the chlorine atom suffers a somewhat greater displacement than that of the corresponding methyl group in β-gutta-percha.

The atomic positions arrived at in the above structures are set out in detail, and appear to afford a reasonable interpretation of the *X*-ray intensities; but owing to the limited nature of the *X*-ray data they can only be regarded as approximate, and may have to be considerably modified or even perhaps drastically altered if more precise data become available. This point is mentioned, but does not appear to be sufficiently stressed, in these papers. It is, however, emphasised by the appearance of another paper by C. J. B. Clews[24] dealing with the structure of polychloroprene. In this paper, not only is there lack of agreement with Bunn regarding the molecular configuration, but even the unit cell is assigned quite different dimensions ($a = 8{\cdot}90$, $c = 12{\cdot}21$, $b = 4{\cdot}70$ A.). It is difficult to reconcile these two investigations. The great need in this field at present is obviously more precise experimental work, rather than further speculation.

Rubber can also be made to crystallise by a homogeneous two-dimensional dilatation, and this state has been examined by means of an interesting *X*-ray study carried out on an inflated rubber balloon by A. Schallamach.[25] Using a monoclinic cell[26] which differs somewhat from that employed by Bunn, Schallamach shows that there is a tendency for the crystallites to arrange themselves with the *b c* plane in the plane of the skin, the *a* axis (8·5 A.) perpendicular, and with a random distribution around *a*.

β-*Isoprenesulphone.*—One promising method whereby further progress may be achieved in the rubber problem lies in the accurate and systematic study of bond lengths and valency angles in relatively simple compounds containing isoprene units or related atomic groupings. Such preliminary reconnaissance should obviously precede any serious frontal attack on the polyisoprene structures themselves, and a good start in this direction has been made by E. G. Cox and G. A. Jeffrey[27] in their analysis of β-isoprenesulphone. This work has been carried out very carefully by quantitative intensity measurements on the crystal, and three-dimensional Patterson and Fourier syntheses, and owing to the presence of the relatively heavy sulphur atom the results are largely independent of any purely chemical evidence.

The two molecules of $C_5H_8O_2S$ in the monoclinic cell ($P2_1/m$) appear to exhibit a plane of symmetry. They have a heterocyclic structure, and the interatomic distances (accurate to ± 0·02 A.) show that resonance must occur between the carbon–carbon bonds in the C_4S ring. The C–C distances in the ring (compare X) are all 1·41 A., the methyl group bond length is normal at 1·54 A., C–S is 1·75 A., and S–O, 1·44 A. The distribution of the four bonds about the sulphur atom is approximately tetrahedral, the O–S–O angle being bisected by the plane of the carbon atoms. It is

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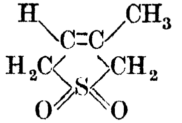
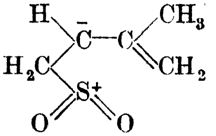
[24] *Proc. Roy. Soc.*, 1942, *A*, **180**, 100.

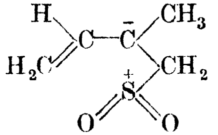
[25] *Nature*, 1942, **149**, 112.

[26] W. Lotmar and K. H. Meyer, *Monatsh.*, 1936, **69**, 115.

[27] *Trans. Faraday Soc.*, 1942, **38**, 241.


(X.)


(XI.)


(XII.)

suggested that the normal state involves resonance between (X) and the ionised forms (XI) and (XII), the three structures making approximately equal contributions. This would involve 33% of double-bond character in the C–C links and lead to a distance very nearly equal to the observed value. Another possibility is that of "hyperconjugation" as discussed recently by R. S. Mulliken, C. H. Riehe, and W. G. Brown,[28] but the observed normal value of the methyl group bond is against this explanation.

The intermolecular approaches are of the approximately normal van der Waals type, *viz.*, 3·45—4·0 A. The successful elucidation of this structure which has now been achieved should have important bearings in connection with the study of vulcanisation processes and rubber chemistry generally.

Protein Structures.—Recent *X*-ray work on keratin and myosin was mentioned last year, and a more complete account has now been published.[29] *X*-Ray studies of some iodinated amino-acids and proteins[30] show that in some cases iodination appears to cause a structural rearrangement.

Some extremely interesting work is now being carried out on the crystal structure of hæmoglobin by M. F. Perutz,[31] based on the earlier work of J. D. Bernal, I. Fankuchen, and M. F. Perutz.[32] When wet crystals of horse methæmoglobin ($a = 109 \pm 0{\cdot}5$, $b = 63{\cdot}8$, $c = 55{\cdot}1$ A., $\beta = 111{\cdot}1°$) are dried they contract by over 30% of their wet volume, and the contraction is found to take place wholly in the *b* plane, the length of the *b* axis remaining unchanged. Further, the contraction can be made to take place slowly and in stages, and the change in the *X*-ray diffraction pattern can be followed. It is found that there are large changes in the intensities of the ($h0l$) reflections in the different states of hydration. Now, by computing these changes in terms of Patterson–Fourier projections, it should be possible to distinguish those features of the structure which are definitely of intramolecular origin from those which are due merely to intermolecular effects. Thus, if the vector maps prepared at different shrinkage stages show peaks which coincide and are of closely similar shape, then it is probable that they belong to the intramolecular type.

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[28] *J. Amer. Chem. Soc.*, 1941, **63**, 41.

[29] W. T. Astbury, *J.*, 1942, 337.

[30] M. Spiegel-Adolf, R. H. Hamilton, and G. C. Henny, *Biochem. J.*, 1942, **36**, 825.

[31] *Nature*, 1939, **143**, 731; 1942, **149**, 491.

[32] *Ibid.*, 1938, **141**, 523.

By proceeding in this way, vector maps for different stages have been prepared and examined. It is concluded from this and other evidence that the hæmoglobin molecules (two per cell) form coherent sheets parallel to the *c* plane (001), with layers of water and possibly ammonium sulphate lying between the protein sheets. On drying, the protein layers move together and slip over one another, thus increasing the monoclinic angle. Each molecule lies on a two-fold symmetry axis and consists either of two sheets 18 A. thick with water and possibly salt between, or of a single rigid sheet 36 A. thick possessing two-fold symmetry. More recent data, and a comparison with the crystal structure of horse oxyhæmoglobin,[33] lead to the view that the molecule is a platelet with a roughly elliptical base, the axis of the ellipse being about 48 by 64 A., and the thickness of the platelet 36 A. This general method of analysis promises to yield further important results.

J. M. Robertson.

[33] *Nature*, 1942, **150**, 324.

ORGANIC CHEMISTRY.

1. INTRODUCTION.

PROGRESS in stereochemistry has in the main continued on existing lines and no striking new developments have been noted. The boundaries of stereochemistry, never very precise, continue to become more fluid. On the one hand, stereochemical work becomes more and more affected by quantitative developments of a physical or mathematical kind, and on the other hand, the bearing of stereochemical considerations on other branches of chemistry becomes increasingly evident. In this Report, no detailed discussion is attempted of recent progress in particular branches of stereochemistry; these have mostly been dealt with in recent years in other reports to which references are given.

Instead, an account is given of the general trend of stereochemical work. The study of atomic and molecular dimensions by physical methods, the quantum mechanical treatment of valency problems and the development of mathematical theories of optical rotatory power are now giving the subject a quantitative basis. On the more qualitative side, the study of various forms of isomerism continues. The use of stereochemical methods in the study of reaction mechanism, particularly in replacement reactions (Walden inversion) and molecular rearrangements, is referred to and a brief survey is attempted of the somewhat related topics of asymmetric transformation, induced optical activity and asymmetric synthesis.

The selection of material is particularly difficult in a report dealing with developments in general methods. In the compilation of this section of the present Report, in spite of both the reduced amount of published matter and the inaccessibility of various journals, this difficulty was ever present; a considerable selection of material was necessary even within the three topics chosen for consideration. The reporter has limited himself to a discussion of, first, boron fluoride catalysis, secondly, some metal enolate condensations and finally a *pot pourri* of generally unrelated reactions chosen because of general interest and general applicability.

Evidence that lignin is largely a phenylpropane derivative has accumulated in recent years as the result of the efforts of H. Hibbert, K. Freudenberg and others, and the Report on lignin deals largely with this theme. After a brief account of extraction methods and such physical evidence as is available, such as studies on the absorption spectrum, the general evidence as to the predominantly aromatic nature of lignin is reviewed. This is followed by an account of the theoretical speculations of K. Freudenberg as to the structure and building up of the lignin molecule as chains of substituted propylphenol residues containing in some instances chroman and in others furan rings, and the experimental evidence adduced in support of this theory. H. Erdtman's idea that lignin is related to dehydro*iso*eugenol and the experimental evidence in favour of this view is then discussed, and the work of H. Hibbert and his school is summarised. This includes the breakdown of lignin by oxidative alkaline degradation to such products as vanillin and syringic aldehyde, and the isolation by ethanolysis of products like α-ethoxypropiovanillone and syringoyl methyl ketone, which with the isolation of propyl*cyclo*hexanols by the hydrogenation of wood and lignins gives strong support for the phenylpropane theory of lignin structure. Hibbert's theory that lignin is essentially a product derived from plant respiratory catalysts is also discussed. The report concludes with a summary of recent attempts to define the type of union between lignin and carbohydrates in wood, if such exists.

The active study of polycyclic aromatic compounds in the last decade has been stimulated by the intrinsic interest of their physico-chemical behaviour, by the cancer-producing activity of many of them (which can now be correlated in general terms with structure), by their relation to (mainly hydroaromatic) natural products, and by their importance in the dye industry. Reinvestigation of coal tar has disclosed the presence of many methyl homologues of naphthalene and phenanthrene, and a variety of polycyclic substances; and destructive hydrogenation of coal or tar oils, followed by dehydrogenation, provides a useful source of pyrene and chrysene. Synthetic methods include, in addition to significant variations and extensions of standard anthracene and phenanthrene syntheses and of the Diels–Alder reaction, numerous processes in which the ends of a four-carbon chain are attached to the *o*-positions of an aromatic nucleus. Difficulties in the preparation and striking abnormalities in the behaviour of 4 : 5-disubstituted phenanthrenes and similar compounds are attributed to spatial interference of the substituents.

In *linearly* but not in *angularly* fused systems, increase in the number of rings results in enhanced chemical reactivity and depth of colour and in increasing stability of the *meso*-dihydro-compounds relatively to the parent hydrocarbons, which are known up to the deep green heptacene, $C_{30}H_{18}$. Various reactions suggest a degree of fixation of double bonds in these substances. The reversible photochemical addition of oxygen, giving a *meso*-peroxide, is a specific property of anthracene systems, whose *meso*-reactivity is further exhibited in their behaviour as dienes in the Diels–Alder reaction with a great variety of partners, and in their ready substitution, notably by reactive diazo-compounds. Much work has been done on substitution and orientation in, among others, phenanthrene, pyrene and chrysene, and it is interesting that carcinogenic hydrocarbons are hydroxylated in the animal body in positions which are not those of normal substitution.

In the heterocyclic series new or improved methods are reported for the synthesis of derivatives of quinoline, thiophen and selenophen, piperidine and tetrahydro(thio)pyran, and of bicyclic systems with a nitrogen atom as bridge-head. The selective hydrogenation of polycyclic systems containing nitrogen rings, the mode of condensation of thionaphthenquinones with thioindoxyls to indigoid dyes, and the transformations of acridones, especially to intensely chemiluminescent derivatives of 5 : 5′-diacridyl, have been carefully studied. G. Heller's formula for indophenine is confirmed.

The systematic investigation of plant constituents has disclosed minor structural novelties in flavan derivatives and their glycosides, and in benzyl*iso*quinoline alkaloids; more notable are the osage orange pigments which contain an *iso*flavone system joined to a terpene residue, and the fused indole and *iso*quinoline structure assigned to *Erythrina* bases. The constitution of retronecine, the commonest basic moiety of the *Senecio* alkaloids, is now largely elucidated. A remarkable toxic polypeptide from the fungus *Amanita phalloides* contains a diastereoisomeride of the common hydroxyproline together with a hydroxytryptophan.

M. P. BALFE.
J. W. COOK.
J. KENYON.
E. G. V. PERCIVAL.
F. S. SPRING.
T. S. STEVENS.

2. STEREOCHEMISTRY.

Stereochemistry was last included in these Reports in 1939.[1] In recent years there have been important developments in the quantitative study of stereochemistry (atomic and molecular dimensions, bond lengths and intervalency angles) as was indicated in 1932 by the inclusion of Stereochemistry in the General and Physical Chemistry Section of these Reports.[2] In 1937 a treatment of the topic on these lines was included in the Organic Chemistry Section.[3] In the Pedler lecture, 1942, W. H. Mills [4] gave a very welcome outline of the theoretical basis of stereochemistry—the relation between the electronic structures of atoms and their valency configurations—in a simplified form, for the encouragement of the organic stereochemist. N. V. Sidgwick and H. M. Powell [5] give a survey of the spatial arrangements of the covalencies of multivalent atoms and their relation to the electronic groups occupied by the valency electrons : they also list the various methods used in the study of atomic structure and molecular configuration. Prominent amongst these methods is *X*-ray crystallography,[6] which, incidentally, has been used to distinguish between racemic mixtures and *meso*-compounds in the αβ-diethyldibenzyl series.[7] W. T. Astbury [8] surveys the application of *X*-ray and other methods to the study of the proteins, one of the numerous applications of stereochemistry.

There is little scope for the organic chemist in these quantitative investigations, though A. Lüttringhaus and collaborators[9] use a chemical method in the investigation of intervalency angles. They determine the number of carbon atoms necessary in chains attached to the two valencies, to permit ring-closure between the two chains. If in a ring of type $X<\begin{smallmatrix}(CH_2)_m\\(CH_2)_n\end{smallmatrix}>CH_2$, the number of carbon atoms ($m + n + 1$) and the carbon valency angle are known, the valency angle of $X<$ can be calculated. When $X = CH_2$, the valency angle $>CH_2$ can be calculated from the number of atoms ($m + n + 2$) in the ring.

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[1] P. Maitland, *Ann. Reports*, 1939, **36**, 247.

[2] N. V. Sidgwick, *ibid.*, 1932, **29**, 64.

[3] L. O. Brockway and T. W. J. Taylor, *ibid.*, 1937, **34**, 196.

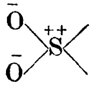
[4] *J.*, 1942, 457.

[5] *Proc. Roy. Soc.*, **1940**, *A*, **176**, 153.

[6] J. M. Robertson, *Ann. Reports*, 1940, **37**, 188; 1941, **38**, 106; G. C. Hampson, *ibid.*, 1940, **37**, 179; H. M. Powell, *ibid.*, 1941, **38**, 99.

[7] C. H. Carlisle and (Miss) D. Crowfoot, *J.*, 1941, 7.

[8] *J.*, 1942, 337.

Though, as the authors observe, the results may be affected by the deformability as well as the magnitude of the angles, they obtain values ($CH_2<$ 112°, $S<$ 110°) which are in harmony with those obtained by other methods. For  they obtain a value of 75°, which, in comparison with the value for $S<$, they suggest indicates repulsion between the two negatively charged oxygen atoms.

Theories of Optical Rotatory Power.

The relation between chemical constitution and optical rotatory power, and the effect of solvents on optical rotatory power, were for many years domains of the organic chemist, whose treatment was necessarily somewhat empirical. Treatments of a more theoretical character are developing. Theories of optical rotatory power have been reviewed by W. J. Kauzmann, J. E. Walter, and H. Eyring,[10] who discuss the interpretation of the effects of temperature, solvents and molecular structure on rotatory power, and by W. J. Kauzmann and H. Eyring.[11] C. O. Beckmann and H. C. Marks[12] give an equation for the influence of dipolar solvents on the rotatory powers of optically active compounds, which is in accord with observations on certain derivatives of (+)-tartaric acid and (−)-menthol, in a variety of mixed solvents. Meanwhile, the organic chemists proceed with the provision of data for eventual digestion by theory. B. K. Singh[13] and M. and A. Singh[14] continue the examination of the relation between chemical constitution and optical rotatory power, and an addition has been made[15] to the somewhat restricted list of compounds to the rotatory dispersion of which a two-term Drude equation (see below) has been fitted. P. A. Levene and A. Rothen[16] discuss the effect of structure on the rotatory dispersion and absorption spectra of substances which contain phenyl or *cyclo*hexyl groups.

The examination of the effect of solvents on rotatory power has continued.

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[9] A. Lüttringhaus and K. Buchholz, *Ber.*, 1940, **73**, 134; A. Lüttringhaus and K. Hauschild, *ibid.*, p. 145.

[10] *Chem. Reviews*, 1940, **26**, 339.

[11] *J. Chem. Physics*, 1941, **9**, 41.

[12] *Ibid.*, 1940, **8**, 827, 831.

[13] B. K. Singh and A. B. Lal, *Proc. Indian Acad. Sci.*, 1940, **12**, *A*, 157.

[14] *J. Indian Chem. Soc.*, 1941, **18**, 89.

[15] R. S. Airs, M. P. Balfe, S. M. Irwin, and J. Kenyon, *J.*, 1942, 531.

[16] *J. Chem. Physics*, 1939, **7**, 975.

A. W. H. Pryde and H. G. Rule [17] report that there is no simple relation between the optical activities and refractive indices of solutions of certain hydrocarbons [(—)-dimenthyl, (—)-dibornyl and (+)- and (—)-*iso*camphanes], giving references to other workers who have suggested that such relationships should exist. They observe that the same conclusion can be drawn from the measurements by J. Kenyon and B. C. Platt [18] of the rotatory powers of solutions of (+)-γ-methyl-*n*-heptane in various solvents. The latter authors point out that their results show the existence of solvent effects on rotatory power, even when solvent and solute are both of non-polar type.

As T. M. Lowry emphasised in his text-book,[19] in investigations of which the main object is the recording of rotatory powers, it is highly desirable that measurements should be made over a wide range of wave-lengths. It is to be hoped that the practice of making observations up to the limit of ultraviolet transmission will develop, and will be supported by the observation of absorption spectra, at least in those cases where the rotatory dispersion shows complexity. Unfortunately, facilities for the measurement of rotatory power outside the visible spectrum are at present available in only a few laboratories.

Stereoisomerism.

The application of adsorption methods to stereochemical problems has received some attention. (Miss) M. M. Jamison and E. E. Turner [20] have described the partial separation of the diastereoisomerides of (—)-menthyl *dl*-mandelate by preferential adsorption on alumina. Separations of optically active forms from racemic mixtures by selective adsorption on optically active solids were referred to in 1939 [1] (G. Karagunis and G. Coumoulos,[21] triethylenediaminochromitrichloride, $\mathrm{Cr\,en_3Cl_3}$, on quartz; and G. M. Henderson and H. G. Rule,[22] *p*-phenylenebisiminocamphor on lactose). R. P. Linstead and collaborators [23] discuss the stereochemistry of catalytic hydrogenation. Using derivatives of diphenic acid and of phenanthrene as substrates, hydrogenation being conducted principally in acetic acid solution in which platinum oxide catalyst is suspended, they conclude that the hydrogen atoms add to one side of the molecule only (*cis*-hydrogenation). *trans*-Hydrogenation is impossible, since the other side of the molecule is protected through adsorption on the surface of the catalyst. This work, though not the first, is probably the most important contribution to the topic.

F. E. Ray and S. Palinchak [24] report the existence of the anion of 9-*aci*-nitro-2-benzoylfluorene in an optically active form, through the separation of its diastereoisomeric brucine salts. It was believed that the centre of asymmetry in such ions is a tercovalent, negatively charged carbon atom linked to the nitrogen atom (as shown in I), but on the whole this structure is improbable (see T. W. J. Taylor and W. Baker[25]). F. E. Ray and S. Palinchak,[24] finding that the anion remains optically active only when the salt contains a molecule of alcohol of crystallisation, have adopted a suggestion of R. L. Shriner and J. H. Young[26] that the configuration of the asymmetric carbon atom is stabilised by the formation of a fourth (co-ordinate) link to the hydroxylic group of the alcohol molecule (II). An alternative, and equally plausible, explanation was put forward by T. W. J. Taylor and W. Baker,[25] *viz.*, that the salt is not formed by substitution, but is an addition compound (III). In the formation of both (II) and (III), the four valencies of the carbon atom need not be disturbed, so the optical activity of the *aci*-nitro-compounds can no longer be regarded as relevant to optical stability of tercovalent carbanions. It is indeed by no means obvious that a structure such as (I) would retain the optical activity of the $C^{\ominus}$ atom. Ten electrons are available for formation of the three bonds of the nitrogen atom. Each bond (including the carbon–nitrogen bond) will, therefore, approximate more closely to a double bond than to a single bond, and the effect of this on the tetrahedral structure of the carbon atom is open to question.

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[17] *J.*, 1940, 345.

[18] *J.*, 1939, 633.

[19] "Optical Rotatory Power," London, 1935.

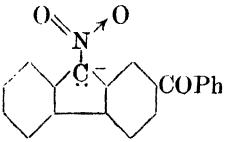
[20] *J.*, 1942, 611.

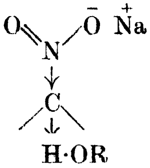
[21] *Nature*, 1938, **142**, 162.

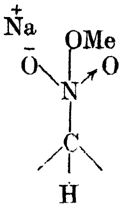
[22] *J.*, 1939, 1568.

[23] *J. Amer. Chem. Soc.*, 1942, **64**, 1985, 1991, 2003, 2006, 2009, 2014, 2022.

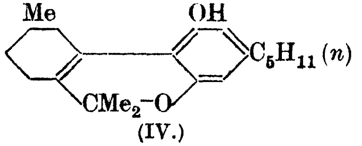
[24] *Ibid.*, 1940, **62**, 2109.

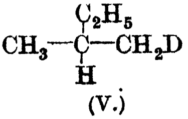

(I.)


(II.)


(III.)

J. B. Kass and S. B. Radlove[27] describe the four diastereoisomeric 9 : 10 : 12-trihydroxystearic acids. R. Adams, C. M. Smith, and S. Lowe,[28] from (+)-3-methyl*cyclo*hexanone (previously described by O. Wallach[29]; see also T. M. Lowry, D. M. Simpson, and C. B. Allsopp[30]), and the (−)-enantiomorph [obtained by resolution of the *dl*-form *via* the (−)-menthylhydrazone], have prepared the (+)- and the (−)-form of 1-hydroxy-6 : 6 : 9-trimethyl-3-*n*-amyl-7 : 8 : 9 : 10-tetrahydro-6-dibenzopyran (IV), which is related to the active principles of marihuana or hashish. They find that the (−)-form of (IV) has a higher narcotic activity than the (+)-form. G. Leaf, A. R. Todd, and S. Wilkinson[31] also have prepared (+)-(IV) from (+)-3-methyl*cyclo*hexanone and found its narcotic activity to be less than that of the *dl*-form.


(IV.)


$$CH_3-\overset{C_2H_5}{\underset{H}{C}}-CH_2D$$
(V.)

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[25] N. V. Sidgwick's "Organic Chemistry of Nitrogen," Oxford, 1937, p. 237.

[26] *J. Amer. Chem. Soc.*, 1930, **52**, 3332.

[27] *Ibid.*, 1942, **64**, 2253.

[28] *Ibid.*, p. 2087.

[29] *Annalen*, 1896, **289**, 340.

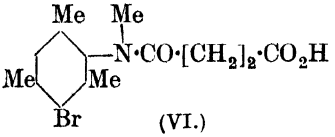
[30] *Proc. Roy. Soc.*, 1937, *A*, **163**, 483.

[31] *J.*, 1942, 185.

J. Chatt and F. G. Mann [32] find confirmatory evidence for the tetrahedral configuration of the 3-covalent arsenic atom, in the isolation of two forms (due to folding along the As–As axis) of 5 : 10-dihydroarsanthren. J. F. Kincaid and F. C. Henriques,[33] on the basis of calculations of the energy required for inversion of the molecules, conclude that $NR'R''R'''$ is irresolvable, on account of ease of racemisation, unless the nitrogen atom forms part of a ring; $PR'R''R'''$ should be resolvable if chemical difficulties can be overcome; $S^{\oplus}R'R''R'''$ is optically stable and racemises by decomposition; $CRR'R''R'''$ can only be racemised by mechanisms which involve the breaking of bonds. These conclusions are in general agreement with experimental evidence.

The search for optical activity due to symmetrically placed hydrogen and deuterium, reviewed in 1939,[1] has continued, though the general trend of the recent papers is to provide confirmatory evidence that optical activity cannot be observed in such compounds. The most unequivocal method is that of H. C. Brown and C. Groot,[34] namely, the introduction of deuterium into an optically active compound in such a way that two of the groups attached to the asymmetric carbon atom become structurally identical but isotopically distinct. Starting from optically active amyl alcohol, they prepared (V); it will be observed that disturbance of the bonds of the asymmetric carbon atom does not occur, so racemisation cannot be due to this cause. The observed rotatory power of their product, in a 1 dm. column, was less than 0·005° and probably less than 0·002°. Other communications on this topic are by G. R. Clemo and G. A. Swann [35] and by H. Erlenmeyer and O. Bitterlin.[36]

Optical activity due to the molecular dissymmetry which arises from restricted rotation [1] continues to receive attention. The fifty-first of the exhaustive studies of R. Adams and collaborators [37] deals with substituted diphenic acids in which the 5- and the 5′-position are joined by bridges containing from 5 to 10 carbon atoms; the optically active forms of these compounds have half-life periods of some 20 minutes. The authors also deal with restricted rotation in arylamines [38] (*e.g.*, VI), in which free rotation about the bond attaching the nitrogen atom to the ring is prevented by interference between the substituents on the nitrogen atom and the two methyl groups which are *o*- to that bond; the compound thus exists in two enantiomorphous forms, in one of which the $CO\cdot[CH]_2\cdot CO_2H$ group is above the plane of the benzene ring and in the



(VI.)

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[32] *J.*, 1940, 1184.

[33] *J. Amer. Chem. Soc.*, 1940, **62**, 1474; other papers which approach the subject in a similar way were reviewed in 1939 (ref. 1).

[34] *J. Amer. Chem. Soc.*, 1942, **64**, 2563.

[35] *J.*, 1942, 370.

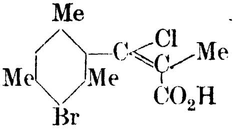
[36] *Helv. Chim. Acta*, 1940, **23**, 207.

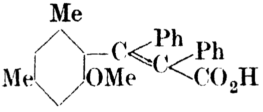
[37] R. Adams and N. Kornblum, *J. Amer. Chem. Soc.*, 1941, **63**, 188.

[38] *Ibid.*, 1940, **62**, 2191; 1941, **63**, 2589; 1942, **64**, 1475.

other, below it. The compounds of this type have half-life periods of some 4 to 30 hours (for other work on this type of restricted rotation, see P. Maitland [1]). R. Adams and collaborators [39] also describe the resolution of compounds of the type (VII), which have half-life periods ranging from 9 minutes to 70 hours. G. Wittig, A. Oppermann, and K. Faber [40] have resolved (VIII), which has a half-life period of 43 minutes.

(VII.)



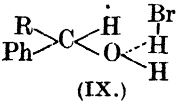


(VIII.)

The Walden Inversion.

The Walden inversion, first observed in 1895, was for many years regarded as a stereochemical mystery, for which, its discoverer observed 34 years later,[41] no satisfactory solution had been found. In the early examples investigated, complicating factors existed, such as the presence of carboxylate groups in the reacting molecules, or heterogeneous reaction conditions (use of silver oxide for hydroxylation of halides), and to these complications many of the early difficulties may be ascribed. Subsequent developments [42] have clarified the general principles which underlie retention of configuration, racemisation or inversion of configuration during aliphatic substitution reactions, and the stereochemical outcome of these reactions can now be used, along with other methods, to elucidate their mechanism.

At the same time, the detailed study of what were once called "Walden inversion reactions" continues. W. Hückel and H. Pietrzok [43] have studied the reaction of phosphorus pentachloride with (—)-menthol, in the presence and in the absence of tertiary bases. P. A. Levene and A. Rothen [44] find that at temperatures below —40° reaction of methyl- and ethyl-phenylcarbinols with hydrogen bromide occurs without change in sign of rotation, or inversion of configuration, possibly owing to formation of an addition complex (IX), which decomposes into the bromide with retention of configuration (this is analogous to the mode of decomposition of certain sulphinoxy chlorides and chloroformates suggested by W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott [45] as an explanation of retention of configuration). P. A. Levene and A. Rothen [44] are of the opinion that certain of their results invalidate some of the conclusions of E. D.



(IX.)

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[39] *J. Amer. Chem. Soc.*, 1940, **62**, 53; 1941, **63**, 1589, 2773; 1942, **64**, 1786, 1791, 1795.

[40] *J. pr. Chem.*, 1941, [ii], **158**, 61.

[41] P. Walden, "Salts, Acids and Bases," London, 1929.

[42] See reviews by H. B. Watson, *Ann. Reports*, 1938, **35**, 218, and E. D. Hughes, *Trans. Faraday Soc.*, 1938, **34**, 202.

[43] *Annalen*, 1939, **540**, 250.

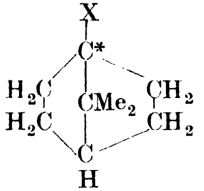
[44] *J. Biol. Chem.*, 1939, **127**, 237; see also P. G. Stevens and N. L. McNiven, *J. Amer. Chem. Soc.*, 1939, **61**, 1295.

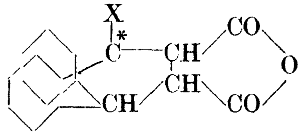
[45] *J.*, 1937, 1252.

Hughes, C. K. Ingold and their collaborators,[45] but this is probably due to their adopting a too limited point of view. As E. D. Hughes, C. K. Ingold, and I. C. Whitfield [46] point out, the effect of solvent and other experimental circumstances on the stereochemical outcome of any given reaction is a combination of the effects on three possibly concurrent reaction mechanisms, which result in inversion of configuration, racemisation, or retention of configuration. It is therefore to be expected that, when the conditions are varied, complicated but not incomprehensible changes in the course of the reaction may occur.

P. D. Bartlett and collaborators [47] show that compounds (X) and (XI)

(X.)

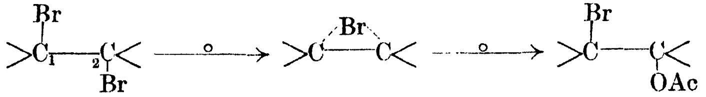




(XI.)

will not undergo certain replacement reactions, such as halogenation of the alcohols (X = OH) or hydrolysis of the halides (X = Cl). This lack of reactivity is attributed to steric factors. Inversion of configuration of the carbon atom (C*) is impossible, because it forms the junction of two rings. The racemisation reaction, which involves separation of a carbonium kation, cannot occur because the carbon atom (C*) cannot adopt the planar configuration which is essential in its kationic state. P. D. Bartlett and L. V. Rosen [48] also ascribe the lack of reactivity of *neo*pentyl halides to steric hindrance of the methyl groups in the *neo*pentyl radical, which prevents the close approach of a reacting ion.

S. Winstein and collaborators [49] report a study of the rôle of neighbouring groups in replacement reactions. They conclude that in the reaction of 2 : 3-dibromobutanes or 1 : 2-dibromo*cyclo*hexanes with silver acetate (in acetic acid), removal of one bromine atom from the dibromide (XII) is accompanied by formation of the intermediate (XIII), which has a (presumably mesomeric) ring structure. The formation of this intermediate and its reaction to give the bromo-acetate (XIV) are both accompanied by inversion of configuration on C_2; these two consecutive inversions necessarily result in retention of configuration. Similarly the reaction of the bromo-acetate (XIV) with silver acetate proceeds through a ring-structured intermediate (XV), which is formed and opened with inversion of configur-



(XII.) (XIII.) (XIV.)

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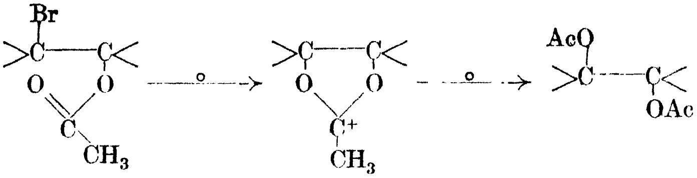
[46] *Nature*, 1941, **147**, 206. [47] *J. Amer. Chem. Soc.*, 1939, **61**, 3184; 1940, **62**, 1183.

[48] *Ibid.*, 1942, **64**, 543; see also A. G. Evans and M. Polanyi, *Nature*, 1942, **149**, 608, 665.

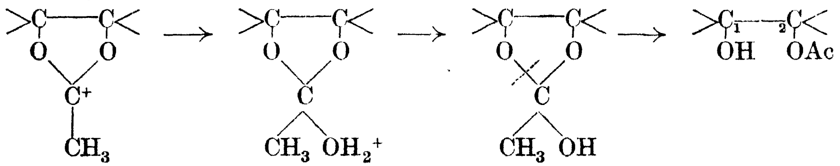
[49] *J. Amer. Chem. Soc.*, 1942, **64**, 2780, 2787, 2791, 2792, 2796.

ation, so that the acetate (XVI) again has the same configuration as the bromide from which it is derived.



(XIV.) (XV.) (XVI.)

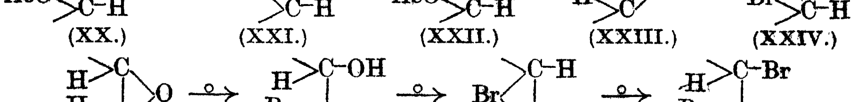
When the solvent contains a small amount of water, a large proportion of the reaction product is monoacetate of inverted configuration. To explain this, it is suggested that, by addition of water, the intermediate (XV) is converted into (XVII), which loses a proton and then, by ring opening as shown by the dotted line in (XVIII), gives the monoacetate (XIX).



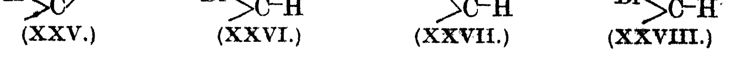
(XV.) (XVII.) (XVIII.) (XIX.)

In (XIX), C_1 has the inverted configuration because it has undergone one inversion reaction [formation of the ring (XV)] and one reaction with retention of configuration (XVIII ⟶ XIX). Since in any of the ring-opening reactions, either the bond to C_1 or that to C_2 may be broken, mixtures of isomers may result if the compounds have the necessary lack of symmetry.

The above mechanisms apply also to the reactions of *trans*-2-acetyl*cyclo*hexyl *p*-toluenesulphonate with silver acetate, and the hypothesis of intermediate ring (XIII) formation is used by the authors to explain retention of configuration in the bromination of 3-bromo-2-butanol with phosphorus tribromide. The assumption that the neighbouring group always intervenes, and that the resulting intermediate is both formed and reacts with inversion of configuration is also used to explain the formation of the *trans*-form of 1 : 2-dibromo*cyclo*hexane by a variety of reactions, *viz.*, the reaction of bromine with *cyclo*hexene, of hydrogen bromide with the *cis*- and the *trans*-diacetate, with *cyclo*hexene oxide, and with the 1-bromo-2-*p*-toluenesulphonate, and the bromohydrins. Two examples, starting from the *trans*-diacetate (XX) and *cyclo*hexene oxide (XXV) must suffice to show the application of the mechanism :



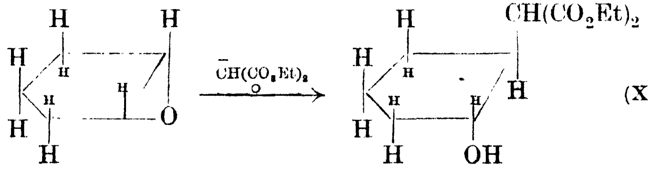
(XX.) (XXI.) (XXII.) (XXIII.) (XXIV.)



(XXV.) (XXVI.) (XXVII.) (XXVIII.)

Neighbouring groups play a particularly important part in substitution reactions in the sugar series.[50] In the alkaline hydrolysis of sugar *p*-toluenesulphonates, an intermediate of ethylene oxide type is formed, and reacts, with the same configurational and isomeric changes described above, if the neighbouring group is *trans*- to the toluenesulphonyl group, and is converted into $>CH\cdot O^{\ominus}$ by the alkali. Such groups are OH, O·COR, and $O\cdot SO_2R$. If the neighbouring group is resistant to the alkali, or *cis*- to the toluenesulphonyl group, the reactivity of the latter is much reduced, and it reacts, if at all, without inversion. G. J. Robertson and W. Whitehead,[51] for example, have found that when 3-*p*-toluenesulphonyl-4-acetyl-6-triphenylmethyl-2-methyl α-methylaltroside is treated with dilute alkali solution, the acetyl group is removed but the toluenesulphonyl group remains. With less dilute alkali, decompositions occur, but in no case is the 3 : 4-anhydro-derivative formed, because there is not, adjacent to the *p*-toluenesulphonyl group, a *trans*-substituent which is converted into $>CH\cdot O^{\ominus}$ by reaction with the alkali (the acetyl group is *cis*- to the 3-toluenesulphonyl group, and the *trans*-2-substituent, methoxyl, is resistant to alkali).

W. E. Grigsby, J. Hind, J. Chanley, and F. H. Westheimer [52] show that inversion of configuration occurs during the opening of the ethylene oxide ring in *cyclo*pentene oxide by reaction with sodiomalonic ester (XXIX ⟶ XXX).



(XXIX.) (XXX.)

Molecular Rearrangements.

Molecular rearrangements form another topic in which the study of stereochemical changes can be used as a mode of investigation. It is established that, when the migrating radical (specifically, the carbon atom therein which breaks one bond and forms another) is optically active, the optical activity is lost in intermolecular rearrangements and retained in intramolecular rearrangements. The occurrence or not of Walden inversion during the intramolecular rearrangement depends on whether the carbon in question carries a sextet or an octet of electrons during its migration. Subsequent to the review of the subject in 1941,[53] the paper by H. I. Bernstein and E. S. Wallis [54] may be noted, wherein are discussed some molecular rearrangements of optically active truxillamic acids.

R. S. Airs, M. P. Balfe, and J. Kenyon [55] describe the rearrangement of γ-methyl-α-ethylallyl alcohol to α-methyl-γ-ethylallyl alcohol (XXXI ⟶ XXXII), which is analogous to the rearrangement of α-phenyl-γ-methylallyl alcohol and its hydrogen phthalate to the corresponding γ-phenyl-α-methylallyl derivatives.[56] An interesting feature of these intramolecular reactions is that in the product of the rearrangement, the asymmetric carbon atom is not the asymmetric atom of the original compound, yet a high degree of optical activity is retained during the rearrangement.

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[50] See review by S. Peat, *Ann. Reports*, 1939, **36**, 258; also H. S. Isbell, *Ann. Rev. Biochem.*, 1940, **9**, 65.

[51] *J.*, 1940, 319.

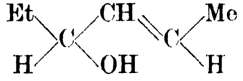
[52] *J. Amer. Chem. Soc.*, 1942, **64**, 2606.

[53] H. B. Watson, *Ann. Reports*, 1941, **38**, 121.

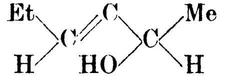
[54] *J. Org. Chem.*, 1942, **7**, 261.

[55] *J.*, 1942, 18; see also M. P. Balfe and J. Kenyon, *Trans. Faraday Soc.*, 1941, **37**, 721.

(XXXI.)



(XXXII.)



Configurational Relationship.

Since the relative configurations of members of series of compounds $^{a}_{b}{>}C{<}^{c}_{X}$, in which X is varied, cannot be deduced directly from the signs of their rotatory powers, the experimental investigation of relative configurations has long been a feature of stereochemical work.[23] In the period under review, P. A. Levene and M. Kuna [57] have deduced the following relations: (i) *propionic series*, (—)-$CH_3\cdot CHR\cdot CO_2H$ and (+)-$CH_3\cdot CHR\cdot CH_2\cdot NH_2$ have the same relative configurations; (ii) *butyric series*, (+)-$CH_3\cdot CH_2\cdot CHR\cdot CO_2H$ and (+)-$CH_3\cdot CH_2\cdot CHR\cdot CH_2\cdot NH_2$ have the same relative configurations (R varies from C_2H_5 to C_6H_{13}); (iii) (—) $^{C_5H_{11}}_{CH_3}{>}CH\cdot[CH_2]_2\cdot CO_2H$, (+) $^{C_5H_{11}}_{CH_3}{>}CH\cdot CH_2\cdot CO_2H$, (—) $^{C_5H_{11}}_{CH_3}{>}CH\cdot CO_2H$ have the same relative configuration.

In this Report, (+) and (—) are used for sign of rotatory power. Though this convention was suggested in 1898,[58] it has not been universally accepted. The present position is that those authors who use (+) and (—) apply them to sign of rotation, and *d* and *l*, if used in conjunction with (+) and (—), refer to relative configuration. When *d* and *l* are used alone, however, it will generally be found that they apply to sign of rotation.

It is to be observed [59] that relative configurations can only be assigned inside series in which only one of the groups attached to the asymmetric carbon atom is variable. If two, or more, groups vary, as in $^{a}_{b}{>}C{<}^{c}_{d}$ (XXXIII) and $^{a}_{b}{>}C{<}^{e}_{f}$ (XXXIV), then (XXXIII) may be converted into (XXXIV) by two routes (c ⟶ e and d ⟶ f, or c ⟶ f and d ⟶ e) and the assignment of relative configuration between the two compounds will depend on the arbitrary choice of one or other of these routes.

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[56] J. Kenyon, S. M. Partridge, and H. Phillips, *J.*, 1937, 207.

[57] *J. Biol. Chem.*, 1941, **140**, 225, 259.

[58] H. Landolt, "Optisches Drehungsvermögen," 2nd ed., 1898; see also 2nd English ed., "Optical Rotatory Power of Organic Substances," 1902.

[59] K. Freudenberg, "Stereochemie," Leipzig, p. 662; see also S. M. Partridge, *J.*, 1939, 1201.

Asymmetric Transformation.

When in a pair of diastereoisomerides (+)A(−)B and (+)A(+)B, the component B is optically unstable, the two forms will differ in stability, so that at equilibrium they will be present in unequal amounts in solution. The subject was reviewed in 1939,[1] largely on the basis of some interesting developments by M. M. Jamison and E. E. Turner,[60] whose work has been continued.[61] In their latest paper,[62] these authors record a case [the brucine salt of 2′-(α-hydroxy*iso*propyl)diphenyl-2-carboxylic acid] where they have been able to observe the " first order " and " second order " transformations (R. Kuhn[63]). The " first order " effect is the establishment of the equilibrium between the diastereoisomerides in solution, and the " second order " effect refers to the case where one isomeride separates from the solution. This development opens up the possibility of further study of the " van't Hoff–Dimroth rule," [64] which relates the relative stability and solubility of a pair of interconvertible isomerides in a given solvent.

Induced Optical Activity.

Rotatory dispersion (variation of rotatory power with wave-length of light) can usually be expressed by a one-term or a two-term Drude equation,[19]

$$[\alpha]_\lambda = k_1/(\lambda^2 - \lambda_1{}^2) \quad \text{or} \quad [\alpha]_\lambda = k_1/(\lambda^2 - \lambda_1{}^2) - k_2/(\lambda^2 - \lambda_2{}^2)$$

in which the constants λ_1 and λ_2 are frequencies characteristic of certain bands in the absorption spectrum of the substance. These " optically active " absorption bands are those which exhibit circular dichroism (unequal absorption of right and left circularly polarised light), and although there may be more than one such anisotropic absorption band associated with each optically active centre in the molecule, bands in the visible or near ultra-violet regions have a dominant effect.[10] Thus it may be stated, though perhaps with a certain degree of over-simplification, that there is usually one term in the Drude equation for each optically active centre in the molecule, though, if there is overlapping between the anisotropic bands associated with different centres of asymmetry, their resultant may be covered by a single term. In some substances, however, a two-term equation is required for the rotatory dispersion, though there is only one formal centre of asymmetry. Since such substances frequently contain groups of the type $>C=O$, $>C=C<$, it has been suggested (see, *e.g.*, T. M. Lowry [65]) that under the influence of the fixed asymmetric centre, a condition of " induced asymmetry" arises in these unsaturated groups, which tend towards a semi-polar character

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[60] *J.*, 1938, 1646. [61] (Miss) M. M. Jamison and E. E. Turner, *J.*, 1940, 264.

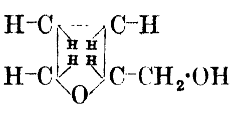
[62] *Idem.*, *J.*, 1942, 437.

[63] *Ber.*, 1932, **65**, 49; as M. M. Jamison and E. E. Turner (ref. 62) point out, the terms are unfortunately chosen, as the phenomena bear no necessary relation to first- and second-order kinetics.

[64] O. Dimroth, *Annalen*, 1910, **377**, 127; 1913, **399**, 91; see also A. Smits, "Theory of Allotropy," London, 1922, p. 69; T. M. Lowry, C. A. H. MacConkey, and H. Burgess *J.*, 1928, 1333.

[65] *Op. cit.* (ref. 19), pp. 374, 389, 411.

$>\overset{\oplus}{C} - \overset{\ominus}{O}$, $>\overset{\oplus}{C} - \overset{\ominus}{C}<$. Though this view may in some cases be valid, the current trend of opinion is away from it. For example, E. Erlenmeyer's claims [66] to have obtained cinnamic acid in optically active forms (in which the "induced asymmetry" has become permanent) are now regarded as resting on an insecure experimental basis. F. Eisenlohr and G. Meier [67] ascribe the optical activity to impurities; other work pointing in the same direction is reviewed by P. D. Ritchie.[68] Further, there are cases, of which (+)-tetrahydrofurfuryl alcohol [15] (XXXV) is an example, in which no such induced asymmetry can be postulated. The alternative hypothesis [69] that, in the presence of a fixed centre of asymmetry, anisotropy may be induced in absorption bands associated with other parts of the molecule, is more generally applicable. The optical activity derived from the induced anisotropy may, in any given region of the spectrum, be an important or even the main contribution to the rotatory power, according to the relative magnitudes of the constants, k_1, k_2, λ_1, λ_2, and so long as the fixed centre of asymmetry remains, the "induced optical activity" remains constant.



(XXXV.)

The hypothesis of "induced anisotropy," though not based on the simple concept of "induced dissymmetry," still depends on the structure of certain groups in the molecule. For example, W. C. Price [70] observes that the properties of the π molecular orbital (which is occupied by two of the electrons of a double bond) give rise to the optical activity of the $>C=O$ bond in certain ketones. T. M. Lowry, D. M. Simpson, and C. B. Allsopp [30] suggest that the induced optical activity of the $>C=O$ groups should be attributed to the non-bonding (unshared) electrons of the oxygen atom, but that it may still be described as induced in the double bond, because "the act of rotation of the plane of polarised light takes place when the electron is raised to its excited state, the orbital of which is located in the double bond."

Asymmetric Synthesis.

Absolute asymmetric synthesis [68] is the synthesis of optically active substances from materials which do not contain sources of asymmetry. T. L. Davies and R. Heggie [71] find that the combination of bromine with trinitrostilbene, in a beam of right circularly polarised light of λ 3600—4500 A. gives a dextrorotatory product. A solution of 0·043 g. of trinitrostilbene in 5 c.c. of glacial acetic acid had, after bromination in this way, a rotatory power of 0·04° in a 1·5 cm. column. The rotatory power is not permanent, possibly owing to the chemical instability of the trinitrostilbene dibromide which is presumed to be the optically active product. Although the observed rotatory power is low, it is of the order of magnitude predicted by an expression [72] based on the circular dichroism and rotatory power of the substance.

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[66] See, *e.g.*, *Biochem. Z.*, 1912, **43**, 445. [67] *Ber.*, 1938, **71**, 1005.

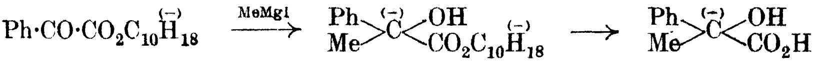
[68] "Asymmetric Synthesis and Asymmetric Induction," Oxford, 1933.

[69] W. Kuhn, *Ber.*, 1930, **63**, 190; W. Kuhn, K. Freudenberg, and J. Wolf, *ibid.*, p. 2370.

[70] *Ann. Reports*, 1939, **36**, 52. [71] *J. Amer. Chem. Soc.*, 1935, **57**, 377, 1622.

Partial asymmetric synthesis [1, 68, 73] was defined by W. Marckwald [74] as a synthesis which produces optically active compounds from substances of symmetrical constitution, optically active substances being used as intermediates, but without any process of fractionation. Processes based on differences between diastereoisomerides (*e.g.*, differences in rate of formation, rate of decomposition, stability or solubility) are mostly excluded by this definition.

A. McKenzie and collaborators [68, 75, 80] have made an extensive study of asymmetric synthesis based on α-ketonic esters. For example,[76] (–)-menthyl benzoylformate (XXXVI), by interaction with a Grignard reagent, gives the ester of atrolactinic acid (XXXVII) and on removal of the (–)-menthol, it is found that the acid (XXXVIII) is optically active.



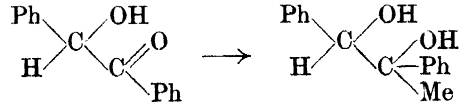
$$\mathrm{Ph{\cdot}CO{\cdot}CO_2C_{10}\overset{(-)}{H}_{18}} \xrightarrow{\mathrm{MeMgI}} \mathrm{\begin{matrix}Ph\\Me\end{matrix}{>}\overset{(-)}{C}{<}\begin{matrix}OH\\CO_2C_{10}\overset{(-)}{H}_{18}\end{matrix}} \longrightarrow \mathrm{\begin{matrix}Ph\\Me\end{matrix}{>}\overset{(-)}{C}{<}\begin{matrix}OH\\CO_2H\end{matrix}}$$

(XXXVI.) (XXXVII.) (XXXVIII.)

A. McKenzie has suggested [77] that the formation of the (—)-acid (XXXVIII) may be primarily due to the existence of (XXXVI) as an unequal mixture of diastereoisomerides, in which the ketonic group exhibits induced dissymmetry, the mutarotation of (XXXVI) which occurs in alcoholic solvents being connected with the attainment of equilibrium between the two forms. M. M. Jamison and E. E. Turner [78] have, however, concluded that the mutarotation is due to solvation or hemiacetal formation. It is more in harmony with current views to ascribe asymmetric synthesis to the same causes as induced anisotropy. The electronic disturbance which causes anisotropy of an absorption band associated with the unsaturated centre may result in an unsymmetrical opening of the double bond during the addition of the entering atom (or ion) and so result in the formation in unequal amounts of the two possible stereoisomeric configurations.

The following reactions may be classed as asymmetric syntheses : formation of only one of the diastereoisomeric glycols from (—)-benzoin by interaction with a Grignard reagent [79] (XXXIX ⟶ XL); formation of optically active methyl αβ-dibromo-β-phenylethyl ketone from (+)-γ-phenyl-α-methyl-

(XXXIX.)



(XL.)

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[72] W. Kuhn and E. Knopf, *Z. physikal. Chem.*, 1930, *B*, **7**, 292.

[73] E. E. Turner, *Ann. Reports*, 1936, **33**, 234.

[74] *Ber.*, 1904, **37**, 1368.

[75] *Ergebn. Enzymforsch.*, 1936, **5**, 58.

[76] A. McKenzie, *J.*, 1904, **85**, 1249.

[77] See, *e.g.*, A. McKenzie and A. D. Wood, *J.*, 1939, 1336.

[78] *J.*, 1941, 538.

[79] A. McKenzie and H. Wren, *J.*, 1910, **97**, 473.

allyl alcohol (XLI $\longrightarrow$ XLII)[80]; and the anionotropic rearrangements of type (XXXI) $\longrightarrow$ (XXXII).[55, 56] There are differences between these

$$\underset{\text{(XLI.)}}{\mathrm{Me{\cdot}CH(OH){\cdot}CH{:}CHPh}} \longrightarrow \mathrm{Me{\cdot}CH(OH){\cdot}CHBr{\cdot}CHBrPh} \longrightarrow \underset{\text{(XLII.)}}{\mathrm{Me{\cdot}CO{\cdot}CHBr{\cdot}CHBrPh}}$$

four types of reaction. In (XXXVI) $\longrightarrow$ (XXXVIII), the original centre of asymmetry is recovered unchanged when the (—)-menthol is removed from the hydroxy-acid by hydrolysis; in (XXXIX) $\longrightarrow$ (XL), the original and the new centre of asymmetry both remain in the final product; in (XLI) $\longrightarrow$ (XLII), the original centre of asymmetry is destroyed so that the optical activity of the new centre can be observed without interference; in (XXXI) $\longrightarrow$ (XXXII), the asymmetry of the original centre is lost at the moment when that of the new centre is formed. These, however, are points of detail, and should not obscure the main fact that in each of the four cases an asymmetric centre is formed in an optically active condition, under the influence of an optically active centre already existing in the molecule.

M. P. B.
J. K.

3. General Methods.

Boron Fluoride Catalysis.

The catalytic activity of boron fluoride has been demonstrated for a variety of reaction types during the last twelve years mainly as a result of the researches of J. A. Nieuwland, G. F. Hennion and their collaborators. In general, boron fluoride compares with aluminium chloride in versatility and in many cases it is superior to the latter in giving higher yields, cleaner products, and increased velocity of reaction. There are, moreover, a number of reactions which are catalysed by boron fluoride but not to an appreciable extent by aluminium chloride.

Addition Complexes.—H. Meerwein[1] has shown that boron fluoride unites with water to give a dihydrate, $BF_3,2H_2O$, which can be distilled without decomposition and is characterised by the formation of crystalline salts with some ethers; the dihydrate adds another mole of boron fluoride to give a monohydrate, BF_3,H_2O, which, however, decomposes on distillation. Similarly with alcohols boron fluoride gives two series of addition complexes. The series $BF_3,2ROH$ can be distilled without decomposition, but the series BF_3,ROH decompose on distillation. These complexes are extremely strong acids. In the case of methyl alcohol, one mole of boron fluoride is absorbed, giving the unstable complex, $BF_3,MeOH$, which is probably methoxyfluoboric acid; it has been characterised[2] as its mercuric salt, $Hg[BF_3,MeO]_2$. Distillation of methoxyfluoboric acid gives a mixture of

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[80] J. Kenyon and S. M. Partridge, *J.*, 1936, 1313.

[1] H. Meerwein and W. Pannwitz, *J. pr. Chem.*, 1934, **141**, 123; H. Meerwein, *Ber.*, 1933, **66**, 411.

[2] V. Gasselin, *Ann. Chim. Phys.*, 1894, [vii], **3**, 5.

$BF_2 \cdot OMe$ and the complex BF_3,Me_2O, which is probably the methyl ester of methoxyfluoboric acid.[3,4] This is a colourless liquid, b. p. 128°, most readily obtained by mixing dimethyl ether and boron fluoride. Ethyl alcohol and diethyl ether behave in the same way; the complex BF_3,Et_2O, a liquid, b. p. 126—127°, is widely employed as a catalyst, since it affords a convenient method for storing boron fluoride and it has not the inherent disadvantages associated with the handling of a toxic gas.

Boron fluoride forms addition complexes with acids, $R \cdot CO_2H,BF_3$ and $(R \cdot CO_2H)_2,BF_3$, esters, $R \cdot CO_2R,BF_3$, and with amides, $R \cdot CO \cdot NH_2,BF_3$.[5,6] With acetic anhydride, boron fluoride yields a complex of diacetoacetic anhydride.[5] These are fuming liquids, or solids, and they can replace boron fluoride as catalyst for many reactions, a remark which also applies to dihydroxyfluoboric acid, $H \cdot B(OH)_2F_2$.[7]

Esterification.—The complex $(CH_3 \cdot CO_2H)_2,BF_3$ is a very efficient catalyst for the preparation of esters from carboxylic acids and alcohols [8] and the complex $CH_3 \cdot CO \cdot NH_2,BF_3$ is a good acetylating agent, reacting vigorously with alcohols [9] and with phenols : [10]

$$CH_3 \cdot CO \cdot NH_2,BF_3 + R \cdot OH \longrightarrow CH_3 \cdot CO_2R + BF_3,NH_3$$

Boron fluoride has been employed as a catalyst in the preparation of cellulose esters.[11]

Esters can readily be obtained by treatment of an acid with an olefin in the presence of a boron fluoride catalyst under mild reaction conditions, the method being applicable to both aliphatic and aromatic carboxylic acids.[12] Camphene and acetic acid give *iso*bornyl acetate [13] and *cyclo*hexene and the same acid give *cyclo*hexyl acetate.[14] The complex BF_3,Et_2O is a particularly active catalyst for this type of esterification.[15]

Interesting observations on the simultaneous nuclear alkylation of aromatic acids during the boron fluoride catalysed esterfication with olefins have been made. Propylene quantitatively esterifies benzoic acid with the

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[3] L. A. O'Leary and H. A. Wenzke, *J. Amer. Chem. Soc.*, 1933, **55**, 2117.

[4] S. Sugden and M. Waloff, *J.*, 1932, 1492.

[5] H. Meerwin and D. Vossen, *J. pr. Chem.*, 1934, **141**, 149.

[6] H. Bowlus and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835; H. Meerwein, *Ber.*, 1933, **66**, 411.

[7] T. B. Dorris, F. J. Sowa, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1938, **60**, 656; J. W. Kroeger, F. J. Sowa, and J. A. Nieuwland, *ibid.*, 1937, **59**, 996; U.S.P. 2,192,015.

[8] H. D. Hinton and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1932, **54**, 2017; F. J. Sowa and J. A. Nieuwland, *ibid.*, 1937, **58**, 271; T. B. Dorris, F. J. Sowa, and J. A. Nieuwland, *ibid.*, 1934, **56**, 2689; D. M. Smith, W. M. D. Bryant, and J. Mitchell, *ibid.*, 1940, **62**, 1, 4, 608.

[9] H. D. Hinton and J. A. Nieuwland, *ibid.*, 1933, **55**, 5052.

[10] U.S.P. 2,036,353.

[11] U.S.P. 2,113,293.

[12] T. B. Dorris, F. J. Sowa, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2689; U.S.P. 2,065,540.

[13] D.R.-P. 589,779.

[14] L. Brunel, *Ann. Chim. Phys.*, 1905, [viii], **6**, 216; H. L. Wunderley and F. J. Sowa, *J. Amer. Chem. Soc.*, 1937, **59**, 1010.

[15] S. V. Zavgorodnii, *Acta Univ. Voronegiensis*, 1938, **10**, [2], 41.

formation of *iso*propyl benzoate, nuclear alkylation not occurring; this ester is stable in the presence of boron fluoride.[12] With salicylic acid, on the other hand, propylene reacts in the presence of boron fluoride to give *iso*propyl salicylate, which when gently warmed in the presence of the catalyst rearranges to 2-hydroxy-3-*iso*propylbenzoic acid. Continued treatment of salicylic acid with propylene in the presence of boron fluoride gives a theoretical yield of *iso*propyl 2-hydroxy-3 : 5-di*iso*propylbenzoate.[16]

Olefins will esterify *p*-nitro- and *o*-chloro-benzoic acids, phenylacetic and furoic acids, but *o*- and *p*-aminobenzoic acids do not react. Propylene, the butylenes and the amylenes all give either *sec.*- or *tert.*-alkyl derivatives—never primary—and *cyclo*propane yields *n*-propyl esters.[17] With the complex BF_3,Et_2O as catalyst, carboxylic acids can be esterified by means of ethers, the catalyst effecting cleavage of the ether: [18]

$$R{\cdot}CO_2H + Et_2O \xrightarrow{BF_3,Et_2O} R{\cdot}CO_2Et + EtOH$$

A similar ether cleavage by means of boron fluoride in the presence of acetic anhydride has been described by H. Meerwein and H. Maier-Hüser: [19]

$$(CH_3{\cdot}CO)_2O + Et_2O \longrightarrow 2CH_3{\cdot}CO_2Et$$

Yet another noteworthy catalysed synthesis of an ester has been described by J. F. McKenna and F. J. Sowa [20] in which a nitrile is treated with an alcohol, the ortho-ester being an intermediate:

$$R{\cdot}CN + 3R'{\cdot}OH \xrightarrow{BF_3} R{\cdot}C(OR')_3 \xrightarrow{BF_3} R{\cdot}CO_2R' + R'_2O$$

Boron fluoride also catalyses the acidolysis of esters.[21]

Syntheses of Acids and Esters.—Employing a boron fluoride catalyst, attractive methods for the preparation of acids and esters have been developed by E. I. du Pont de Nemours. Carboxylic acids are obtained directly from alcohols and carbon monoxide at 125—180°/*ca.* 500 atms., the catalyst consisting of boron fluoride and a limited amount of water. Methyl alcohol [22] and ethyl alcohol [23] give acetic and propionic acids respectively. The method, which is applicable to polyhydric alcohols, ethylene glycol yielding succinic acid, can also be applied to olefins, ethylene when treated with carbon monoxide under similar reaction conditions giving propionic acid.[24] A striking development of this method is the preparation of esters by the interaction of an ether and carbon monoxide, dimethyl and diethyl ethers giving methyl acetate and ethyl propionate respectively.[25]

Synthesis of Nitriles and Substituted Amides.—Acid amides are converted into nitriles when treated with boron fluoride. Thus treatment of acetamide with the complex $CH_3{\cdot}CO{\cdot}NH_2,BF_3$ in the presence of a small quantity of a carboxylic acid yields acetonitrile :

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[16] W. J. Croxall, F. J. Sowa, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2054; *J. Org. Chem.*, 1937, **2**, 253.

[17] T. B. Dorris and F. J. Sowa, *J. Amer. Chem. Soc.*, 1938, **60**, 358.

[18] G. F. Hennion, H. D. Hinton, and J. A. Nieuwland, *ibid.*, 1933, **55**, 2857.

[19] *J. pr. Chem.*, 1932, **134**, 51.

[20] *J. Amer. Chem. Soc.*, 1938, **60**, 124.

[21] F. J. Sowa, *ibid.*, p. 654.

[22] U.S.P. 2,135,448; 2,135,451—2 and —3.

[23] U.S.P. 2,170,825; 2,162,459; 2135,454; B.P. 536,422; 516,477.

[24] U.S.P. 2,135,459.

[25] U.S.P. 2,135,450; 2,135,449; 2,135,447.

$$CH_3{\cdot}CO{\cdot}NH_2,BF_3 + CH_3{\cdot}CO{\cdot}NH_2 \xrightarrow{AcOH} Me{\cdot}CN + Me{\cdot}CO_2H + BF_3,NH_3$$

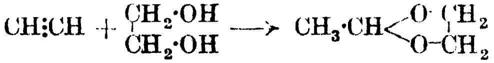
The complex $Me{\cdot}CO{\cdot}NH_2,BF_3$ can also be used for preparing substituted acetamides [26] by interaction with bases :

$$R{\cdot}NHR' + Me{\cdot}CO{\cdot}NH_2,BF_3 \longrightarrow NRR'{\cdot}CO{\cdot}Me + BF_3,NH_3$$

Mercury-catalysed Additive Reactions of Acetylenic Hydrocarbons.—The complexes $MeOH,BF_3$ (methoxyfluoboric acid) and Et_2O,BF_3 are much superior to sulphuric acid or any other acid in catalysing interaction between acetylene and its derivatives and hydroxyl-containing compounds in the presence of mercuric oxide. These complexes are stable, readily dissolve mercuric oxide, and are effective in very low concentrations.[27] In the presence of this mixed catalyst, methyl alcohol readily reacts with acetylene and monoalkylacetylenes, yielding dimethylacetal [28] and dimethylketals [29, 30] respectively :

$$R{\cdot}C{:}CH + MeOH \xrightarrow[HgO]{BF_3,Et_2O} R{\cdot}C(OMe)_2{\cdot}CH_3$$

The same catalyst being used, ethylene glycol reacts with acetylene with production of a dioxole derivative : [31]



$$CH{:}CH + \begin{matrix} CH_2{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{matrix} \longrightarrow CH_3{\cdot}CH{<}\begin{matrix} O{-}CH_2 \\ | \\ O{-}CH_2 \end{matrix}$$

The addition of monohydric alcohols other than methanol cannot be successfully effected by this catalyst, but the applicability of the method is considerably increased if the catalyst contains a small amount of trichloroacetic acid. With this modified catalyst, straight-chain primary alcohols (*e.g.*, EtOH, *n*-PrOH, *n*-BuOH, *n*-pentanol and *n*-hexanol) readily add to alkylacetylenes with formation of the corresponding ketal, but the addition of branched-chain or *iso*-alcohols to alkylacetylenes cannot be achieved.[32] The trichloroacetic acid-promoted catalyst is also of value in the condensation of polyhydric alcohols and α-hydroxy-acids with alkylacetylenes; [33] thus α-hydroxy*iso*butyric acid and butylacetylene give 2 : 5 : 5-trimethyl-2-butyl-1 : 3-dioxol-4-one :

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[26] F. J. Sowa and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1937, **59**, 1202.

[27] J. A. Nieuwland, R. R. Vogt, and W. L. Foohey, *ibid.*, 1930, **52**, 1018; T. H. Vaughn, H. Bowlus, and J. A. Nieuwland, *Proc. Indiana Acad. Sci.*, 1931, **40**, 203.

[28] H. D. Hinton and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1930, **52**, 2892.

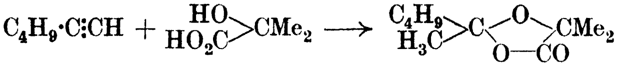
[29] D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *ibid.*, 1934, **56**, 1384.

[30] G. F. Hennion, D. B. Killian, T. H. Vaughn, and J. A. Nieuwland, *ibid.*, p. 1130.

[31] T. H. Vaughn, *Proc. Indiana Acad. Sci.*, 1933, **42**, 127; F. G. Hennion, D. B. Killian, T. H. Vaughn, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 1130.

[32] D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 80.

[33] *Idem*, *ibid.*, p. 1658.



$$C_4H_9{\cdot}C{\vdots}CH + \genfrac{}{}{0pt}{}{HO}{HO_2C}{>}CMe_2 \longrightarrow \genfrac{}{}{0pt}{}{C_4H_9}{H_3C}{>}C{<}\genfrac{}{}{0pt}{}{O}{O-CO}{>}CMe_2$$

Alcohols also add to acetylenic alcohols in the presence of a trichloroacetic acid-promoted $BF_3,Et_2O/HgO$ catalyst; thus dimethylethynylcarbinol yields 3 : 3-dimethoxy-2-methyl-2-butanol, hydrolysis of which with dilute mineral acid gives 2-hydroxy-2-methyl-3-butanone :[34]

$$OH{\cdot}CMe_2{\cdot}C{\vdots}CH + MeOH \longrightarrow CMe_2(OH){\cdot}CMe(OMe)_2 \longrightarrow CMe_2(OH){\cdot}COMe$$

A general mechanism for mercury–boron fluoride catalysis has been suggested by G. F. Hennion, R. R. Vogt, and J. A. Nieuwland;[35] one important experimental observation in this connection is the ease of addition of methyl alcohol to dialkylacetylenes, *e.g.*,

$$C_5H_{11}{\cdot}C{\vdots}CMe \xrightarrow[MeOH]{BF_3/HgO} C_5H_{11}{\cdot}C(OMe)_2{\cdot}CH_2Me$$

from which it is concluded that the intermediate formation of a mercury acetylide is not a prerequisite of reaction.[36]

The catalysed addition of methyl alcohol to vinylacetylene (I) is particularly interesting. In the presence of the $BF_3,Et_2O/HgO$ catalyst (best results being obtained in the presence of trichloroacetic acid promoter) three moles of methyl alcohol react with formation of a methoxy-dimethylketal[37] (III). The reaction probably involves a primary 1 : 4-addition, followed by rearrangement of the allene to the acetylene (II), which reacts further to give the methoxyketal (III) (2 : 2 : 4-trimethoxybutane) :[38]

$$\text{(I.)}\ CH_2{:}CH{\cdot}C{\vdots}CH \xrightarrow{MeOH} [MeO{\cdot}CH_2{\cdot}CH{:}C{:}CH_2] \longrightarrow$$

$$\text{(II.)}\ MeO{\cdot}CH_2{\cdot}C{\vdots}CMe \xrightarrow{MeOH} MeO{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(OMe)_2\ \text{(III.)}$$

The last step has been experimentally realised,[39] and the mechanism receives considerable support from the facts that allyl alkylacetylenes (IV) react with methanol in the presence of catalyst to give unsaturated ketals (V), the ethylenic linkage remaining unchanged,[40] and that methyl vinyl ketone (VI) readily adds methanol in the presence of the same catalyst to yield methyl β-methoxyethyl ketone (VII) (4-methoxy-2-butanone).[41] The method of preparation of the boron fluoride–mercuric oxide catalyst is of particular importance in this type of addition to a vinylacetylene. A $BF_3,Et_2O/HgO$ catalyst promoted by trichloroacetic acid being used, the method is limited to the addition of methyl alcohol. If the catalyst, however, is prepared with methyl alcohol [BF_3,Et_2O is dissolved in methyl alcohol and then warmed with mercuric oxide, the mercuric salt of methoxyfluoboric acid, $Hg(MeO{\cdot}BF_3)_2$, being formed] and promoted with trichloroacetic acid, the higher alcohols can be successfully added to vinylacetylene (and its homologues) to give 2 : 2 : 4-trialkoxybutanes.[42]

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[34] J. F. Froning and G. F. Hennion, *J. Amer. Chem. Soc.*, 1940, **62**, 653; H. Scheibler and A. Fischer, *Ber.*, 1922, **55**, 2903.

[35] *J. Org. Chem.*, 1936, **1**, 159.

[36] G. F. Hennion and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1935, **57**, 2006.

[37] D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *ibid.*, 1934, **56**, 1786.

[38] D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *ibid.*, 1936, **58**, 892.

[39] G. F. Hennion and J. A. Nieuwland, *ibid.*, 1935, **57**, 2006.

[40] D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *ibid.*, 1936, **58**, 1658.

[41] U.S.P. 2,010,828.

Acetylene and alkylacetylenes also add carboxylic acids in the presence of a boron fluoride–mercuric oxide catalyst,[43] the substituted vinyl ester

$$\text{(IV.)}\quad CH_2{:}CH{\cdot}CH_2{\cdot}C{\vdots}CR + 2MeOH \longrightarrow CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(OMe)_2R\quad \text{(V.)}$$

$$\text{(VI.)}\quad CH_2{:}CH{\cdot}COMe + MeOH \longrightarrow MeO{\cdot}CH_2{\cdot}CH_2{\cdot}COMe\quad \text{(VII.)}$$

(VIII) being first formed. A second addition occurs[44] probably through the ester (IX), leading to a methyl ketone and an acid anhydride.[45] The reaction can be controlled to give good yields of either the vinyl ester or the

$$R{\cdot}CO_2H + R'{\cdot}C{\vdots}CH \longrightarrow \underset{\text{(VIII.)}}{R{\cdot}CO{\cdot}O{\cdot}CR'{:}CH_2} \xrightarrow{R{\cdot}CO_2H}$$

$$\text{(IX.)}\quad [(R{\cdot}CO{\cdot}O)_2CR'Me] \longrightarrow (R{\cdot}CO)_2O + R'{\cdot}COMe$$

ketone–anhydride mixture. In the case of the vinyl ester, boron fluoride in the presence of hydrogen fluoride is an effective promoter of the mercury catalyst.[46]

Carboxylic acids are also added to vinylacetylenes in the presence of a trichloroacetic acid-promoted $BF_3,Et_2O/HgO$ catalyst; *e.g.*, vinylacetylene and acetic acid yield the acetate of $\Delta^{1:3}$-butadien-2-ol.[47]

Polymerisation of Ethylenic Hydrocarbons.—The catalytic polymerisation of ethylenic hydrocarbons was first observed by A. Butlerow and W. Gorianow[48] in 1873, but more than fifty years elapsed before this catalytic activity attracted attention. In 1927, M. Otto[49] showed that boron fluoride catalyses the polymerisation of both ethylene and propylene[50] and that this polymerisation is promoted by the addition of finely divided metals such as nickel. Polymerisation of *iso*butene occurs in the presence of a variety of acidic catalysts, the most effective being boron fluoride, aluminium chloride and titanium chloride.[51] The reaction with boron fluoride takes place with almost explosive violence and is among the most rapidly completed of organic reactions. Under suitable conditions a practically quantitative yield of a rubber-like polymer is produced in a fraction of a second; a polymer of molecular weight greater than 400,000 can be obtained.[52] This reaction has an added theoretical interest in that the velocity of reaction is not apparently decreased by lowering the temperature and the molecular weight of the polymer is greater the lower the reaction temperature. The presence of very small quantities of di*iso*butylene decreases both the yield and the molecular weight of the polymer, indicating that the normal dimer cannot be present either during or preceding the polymerisation process. Tri*iso*butylene has a similar effect and neither it nor the dimer can be catalytically polymerised to high molecular weight products. The boron fluoride catalyst is very readily poisoned by small amounts of hydrogen halides, an effect which is probably due to the formation of dimer and consequent inhibition of the true polymerisation.

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[42] R. O. Norris, J. J. Verbane, and G. F. Hennion, *J. Amer. Chem. Soc.*, 1939, **61,** 887.

[43] G. F. Hennion, D. B. Killian, T. H. Vaughn, and J. A. Nieuwland, *ibid.*, 1934, **56,** 1130.

[44] G. F. Hennion and J. A. Nieuwland, *ibid.*, p. 1802.

[45] D.R.-P. 590,237.

[46] U.S.P. 1,912,608.

[47] J. H. Werntz, *J. Amer. Chem. Soc.*, 1935, **57,** 204.

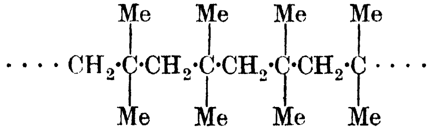
[48] *Annalen,* 1873, **169,** 147.

[49] *Brennstoff-Chem.*, 1927, **8,** 321.

[50] U.S.P. 2,183,503; B.P. 293,487.

[51] M. Otto and M. Mueller-Cunradi, U.S.P. 2,084,501; F. A. Howard, U.S.P. 2,049,062; P. K. Frolich, U.S.P. 2,109,772; D.R.-P. 278,486; H. C. Zimmern and E. W. Carlson, U.S.P. 2,074,093; H. G. Schneider, U.S.P. 2,131,196.

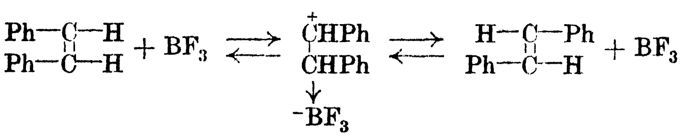
To obtain efficient temperature control, an inert solvent can be employed and it is observed that the molecular weight of the polymer produced increases with the amount of diluent [54] up to a limiting concentration of approximately 80% diluent by volume. Further dilution leads to a dramatic decrease in the molecular weight. R. M. Thomas and his associates [53] believe that the polymer has a head-tail structure with one terminal ethylenic linkage :



$$\cdots\cdot CH_2{\cdot}\underset{Me}{\overset{Me}{C}}{\cdot}CH_2{\cdot}\underset{Me}{\overset{Me}{C}}{\cdot}CH_2{\cdot}\underset{Me}{\overset{Me}{C}}{\cdot}CH_2{\cdot}\underset{Me}{\overset{Me}{C}}\cdots\cdot$$

The estimation of unsaturation (based upon the average molecular weight) agrees with this hypothesis.

Concerning the mechanism of polymerisation it has been suggested [55] that the catalytic activity of boron fluoride involves the activation of the ethylenic link by association with the catalyst. A natural consequence of this mechanism is that boron fluoride should establish an equilibrium between suitable *cis-trans* isomers. It has been shown that boron fluoride does in fact convert *cis*-stilbene into an equilibrium mixture containing 92·2% of the *trans* isomer : [56]



$$\begin{array}{l}Ph-C-H\\ Ph-C-H\end{array} + BF_3 \rightleftarrows \begin{array}{c}\overset{+}{C}HPh\\ CHPh\\ \downarrow\\ {}^{-}BF_3\end{array} \rightleftarrows \begin{array}{l}H-C-Ph\\ Ph-C-H\end{array} + BF_3$$

Alkylation.[57]—A solution of boron fluoride in sulphuric acid catalyses the alkylation of aromatic hydrocarbons by olefins.[58] With propylene, *iso*propylbenzenes are obtained, the di*iso*propylbenzene fraction being almost entirely the *p*-isomer, whereas in the corresponding alkylation using aluminium chloride, the *m*-isomer is the major dialkyl-product.[59] Aromatic hydrocarbons can also be alkylated by means of alcohols in the presence of boron fluoride; since *n*-propyl alcohol and *iso*propyl alcohol both yield *iso*propylbenzenes and *n*-butyl alcohol and *sec.*-butyl alcohol both yield *sec.*-butylbenzenes, J. F. McKenna and F. J. Sowa [59a] conclude that the reaction proceeds by dehydration of the alcohol to an olefin and addition of benzene to the latter according to the Markownikoff rule. Later, N. F. Toussant and G. F. Hennion [60] showed that such alkylations are facilitated by the presence of dehydrating agents such as phosphoric oxide, sulphuric acid, and benzenesulphonic acid, the effect of which is most marked in the case of primary alcohols. Boron fluoride likewise catalyses the alkylation of naphthalene by means of alcohols, the products being β-alkylnaphthalenes with the exception of the case of benzyl alcohol, which yields mainly α-benzylnaphthalene.[61] The dehydration mechanism is contested by C. C. Price and M. Lund,[62] who show that alkylation of benzene with *d*-*sec.*-butyl alcohol in the presence of boron fluoride yields *sec.*-butylbenzene which is lævorotatory, and also by C. C. Price and J. M. Ciskowski.[61] The latter authors show that *cyclo*hexanol is unaffected by boron fluoride under conditions under which *cyclo*hexylation of naphthalene by means of this alcohol proceeds rapidly.

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[52] R. M. Thomas, J. C. Zimmern, L. B. Turner, R. Rosen, and P. K. Frolich, *Ind. Eng. Chem.*, 1940, **32**, 299.

[53] R. M. Thomas, W. J. Sparks, P. K. Frolich, M. Otto, and M. Mueller-Cunradi, *J. Amer. Chem. Soc.*, 1940, **62**, 276.

[54] U.S.P. 2,176,194.

[55] C. C. Price and J. M. Ciskowski, *J. Amer. Chem. Soc.*, 1938, **60**, 2499.

[56] C. C. Price and M. Meister, *ibid.*, 1939, **61**, 1595.

[57] See also *Ann. Reports*, 1941, **38**, 118.

Aromatic hydrocarbons can also be alkylated by means of ethers [63] and esters [64] in the presence of boron fluoride.

Phenols are readily alkylated by means of ethylenic hydrocarbons in the presence of boron fluoride. Propylene and phenol give phenyl *iso*propyl ether,[65] which on standing in contact with the catalyst rearranges to 2-*iso*propylphenol; at 40°, the major product is 2 : 4 : 6-tri*iso*propylphenyl *iso*propyl ether.[66] Phenols can also be alkylated by means of alcohols in the presence of boron fluoride,[67] and by means of ethers with BF_3,Et_2O as catalyst;[68] methylation of phenol with BF_3,Me_2O can be enforced to give pentamethylanisole in high yield.[69, 63]

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[58] S. J. Slanina, F. J. Sowa, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1935, **57**, 1574; H. L. Wunderley, F. J. Sowa, and J. A. Nieuwland, *ibid.*, 1937, **58**, 271; V. N. Ipatieff and A. V. Grosse, *ibid.*, 1936, **59**, 2339; V. N. Ipatieff, B. B. Corson, and H. Pines, *ibid.*, p. 919.

[59] T. M. Berry and E. E. Reid, *ibid.*, 1927, **49**, 3142.

[59a] *Ibid.*, 1937, **59**, 470.

[60] *Ibid.*, 1940, **62**, 1145.

[61] *Ibid.*, 1938, **60**, 2499.

[62] *Ibid.*, 1940, **62**, 3105.

[63] M. J. O'Connor and F. J. Sowa, *ibid.*, 1938, **60**, 125.

[64] J. F. McKenna and F. J. Sowa, *ibid.*, 1937, **59**, 1204.

[65] T. B. Dorris, F. J. Sowa, and J. A. Nieuwland, *ibid.*, 1934, **56**, 2689.

[66] F. J. Sowa, H. D. Hinton, and J. A. Nieuwland, *ibid.*, 1932, **54**, 2019; 1933, **55**, 3402.

[67] F. J. Sowa, G. F. Hennion, and J. A. Nieuwland, *ibid.*, 1935, **57**, 709; J. F. McKenna and F. J. Sowa, *ibid.*, 1938, **60**, 124.

[68] G. F. Hennion, H. D. Hinton, and J. A. Nieuwland, *ibid.*, 1933, **55**, 2857.

[69] A. J. Kolka and R. R. Vogt, *ibid.*, 1939, **61**, 1463.

V. N. Ipatieff and A. V. Grosse [70] have shown that in the presence of water and finely divided nickel, boron fluoride catalyses a reaction between olefins and paraffins whereby higher paraffins are produced :

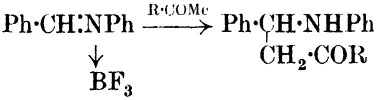
$$\geqslant CH + >C{:}C< \longrightarrow \geqslant C-\overset{|}{\underset{|}{C}}-CH<$$

a reaction which is more conveniently effected by means of sulphuric acid.[71] Olefins have also been used in the presence of boron fluoride to alkylate alicyclic hydrocarbons.[72]

Miscellaneous Reactions.—In the presence of a boron fluoride catalyst alcohols react with cyclic oxides to give a monoether of a diol; ketones and aldehydes also react with cyclic oxides in the presence of boron fluoride, yielding ketals and acetals respectively.[73] Boron fluoride also catalyses a reaction between an olefin and a glycol to give a monoether of the glycol,[74] and in the presence of the same catalyst methyl alcohol adds to trimethylethylene thus : [75]

$$CHMe{:}CMe_2 + MeOH \longrightarrow CH_2Me{\cdot}CMe_2{\cdot}OMe$$

A preparation of amino-ketones from Schiff bases has been described by H. R. Snyder, H. A. Kornberg, and J. R. Romig.[76] Thus benzylideneaniline reacts with BF_3,Et_2O to yield a complex, which rapidly reacts with a methyl ketone, forming an amino-ketone :



$$\underset{\downarrow \atop BF_3}{Ph{\cdot}CH{:}NPh} \xrightarrow{R{\cdot}COMe} \underset{\quad CH_2{\cdot}COR}{Ph{\cdot}\overset{}{\underset{|}{C}}H{\cdot}NHPh}$$

In the presence of boron fluoride, acetic anhydride condenses with acetophenone and with acetone to give benzoylacetone and acetylacetone respectively.[5]

An interesting observation has been made by D. S. Breslow and C. R. Hauser,[77] who show that boron fluoride can replace basic condensing reagents in Claisen, aldol and Michael type condensations.

Boron fluoride is a very effective catalyst for the sulphonation and nitration of aromatic hydrocarbons and their derivatives.[78]

Metal Enolate Condensations.

Sodium Triphenylmethyl.—Esters of the type $CHR_2{\cdot}CO_2R'$ fail to undergo the normal Claisen condensation in the presence of sodium ethoxide;[79] using sodium triphenylmethyl, however, W. Schlenk, H. Hillemann, and I. Rodloff[80] prepared the sodium enolate of methyl diphenylacetate and showed that, by treatment of the product with acid chlorides or with alkyl halides, the corresponding acyl- or alkyl-diphenylacetic ester was produced. C. R. Hauser and W. B. Renfrow [81] find that this reaction is generally applicable to disubstituted acetic esters; for example, in the presence of sodium triphenylmethyl, ethyl *iso*butyrate yields ethyl *iso*butyryl*iso*butyrate :

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[70] *J. Amer. Chem. Soc.*, 1935, **57**, 1616.

[71] A. E. Dunstan and S. F. Birch, *Trans. Faraday Soc.*, 1939, **35**, 1013; A. E. Dunstan, *Nature*, 1940, **46**, 186.

[72] V. N. Ipatieff, V. M. Komarewsky, and A. V. Grosse, *J. Amer. Chem. Soc.*, 1935, **57**, 1722.

[73] A. A. Petrow, *J. Gen. Chem. Russia*, 1940, 981.

[74] U.S.P. 2,198,046.

[75] U.S.P. 2,197,023.

[76] *J. Amer. Chem. Soc.*, 1939, **61**, 3556.

[77] *Ibid.*, 1940, **62**, 2385, 2389, 2611.

[78] R. J. Thomas, W. F. Anzilotti, and G. F. Hennion, *Ind. Eng. Chem.*, 1940, **32**, 408.

[79] S. M. McElvain, *J. Amer. Chem. Soc.*, 1929, **51**, 3127.

$$\mathrm{CHMe_2{\cdot}CO_2Et + CPh_3{\cdot}Na \longrightarrow [CMe_2{\cdot}CO_2Et]Na}\ (\mathrm{I.}) + \mathrm{CHPh_3}$$
$$\mathrm{[CMe_2{\cdot}CO_2Et]Na + CHMe_2{\cdot}COX \longrightarrow \underset{(II.)}{CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et} + NaX}$$

The sodium enolate (I) will also condense with *iso*butyryl chloride to yield the same ester (II).[82] The ester (II) yields a sodium enolate when treated with sodium triphenylmethyl and this on treatment with acetyl and *iso*butyryl chlorides gives the diketo-esters $\mathrm{Me{\cdot}CO{\cdot}CMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et}$ (III) and $\mathrm{CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et}$ (IV) respectively.[83] (III) is not changed by treatment with sodium triphenylmethyl, but (IV) is cyclised to hexamethylphloroglucinol, a reaction not accomplished by the weaker base, sodium ethoxide.

Sodium triphenylmethyl has been widely employed in the preparation of the sodium enolates of esters and anhydrides.[84] Attention is directed to two general methods that have been developed by C. R. Hauser and his associates. First, trisubstituted acetic acids or their esters can be obtained by treatment of a disubstituted acetic ester with sodium triphenylmethyl, followed by treatment of the sodium enolate with an alkyl halide :[85]

$$\mathrm{CHR_2{\cdot}CO_2Et + CPh_3Na \longrightarrow [CR_2{\cdot}CO_2Et]Na + CHPh_3}$$
$$\mathrm{[CR_2{\cdot}CO_2Et]Na + R'X \longrightarrow CR_2R'{\cdot}CO_2Et + NaX}$$

Secondly, the ethyl acetoacetate ketone synthesis has been extended by B. E. Hudson and C. R. Hauser [86] to allow of the preparation of ketones of the type $\mathrm{R'{\cdot}CO{\cdot}CHR_2}$. A disubstituted acetic ester is converted into its sodium enolate by means of sodium triphenylmethyl; treatment of the enolate with an acid chloride gives an αα-disubstituted β-keto-ester, hydrolysis of which gives the required ketone :

$$\mathrm{[CR_2{\cdot}CO_2Et]Na + R'{\cdot}COCl \longrightarrow R'{\cdot}CO{\cdot}CR_2{\cdot}CO_2Et \xrightarrow{H_2O} R'{\cdot}CO{\cdot}CHR_2}$$

Alkyl Carbonates.—The carbalkoxylation of ethyl acetate by means of ethyl carbonate had been attempted unsuccessfully by W. Wislicenus.[87]

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[80] *Annalen*, 1931, **487**, 135.

[81] *J. Amer. Chem. Soc.*, 1937, **59**, 1823; 1938, **60**, 463; C. R. Hauser, *ibid.*, 1938, **60**, 1957; B. E. Hudson, R. H. Dick, and C. R. Hauser, *ibid.*, p. 1960.

[82] *Organic Syntheses*, 1939, **19**, 44.

[83] B. E. Hudson and C. R. Hauser, *J. Amer. Chem. Soc.*, 1939, **61**, 3567.

[84] E. Müller, *Annalen*, 1931, **491**, 251; E. Müller, H. Gawlick, and W. Kreutzmann, *ibid.*, 1934, **515**, 97; B. E. Hudson, R. H. Dick, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1938, **60**, 1960; C. R. Hauser and D. S. Breslow, *ibid.*, 1939, **61**, 793.

[85] R. E. Hudson and C. R. Hauser, *J. Amer. Chem. Soc.*, 1940, **62**, 2457.

[86] *Ibid.*, 1941, **63**, 3156, 3163.

[87] *Ber.*, 1887, **20**, 2930; 1894, **27**, 795; *Annalen*, 1888, **246**, 313.

Later, by a modification of the reaction conditions and using powdered sodium as condensing agent, H. Lux [88] obtained the required ethyl malonate in 18% yield, and a similarly low yield of ethyl phenylmalonate was obtained from ethyl phenylacetate.[89] More recently, better yields have been obtained in this type of carbalkoxylation reaction by using potassium or alloys of potassium and sodium.[90] A. C. Cope and S. M. McElvain [91] and R. Connor [92] showed that malonic esters undergo alcoholysis when heated in the presence of sodium ethoxide; *e.g.*,

$$Ph{\cdot}CH(CO_2Et)_2 + EtOH \xrightarrow{NaOEt} Ph{\cdot}CH_2{\cdot}CO_2Et + CO(OEt)_2$$

which is a reversal of the carbalkoxylation reaction. Recognising this fact, V. H. Wallingford and his co-workers [93] have developed a fairly general method for the preparation of substituted malonic esters from monocarboxylic esters. The essential features of the new procedure are that the alcohol formed is removed from the reaction mixture by distillation [94] and that an excess of alkyl carbonate is employed as solvent. Carbalkoxylation of ethyl acetate with ethyl carbonate gives mainly tricarbethoxymethane. On the other hand, C. R. Hauser, B. Abramovitch, and J. T. Adams [95] have shown that, if the sodium enolates of *tert.*-butyl acetate and *tert.*-butyl propionate (prepared by means of sodium triphenylmethyl) are treated with ethyl carbonate, the mixed esters ethyl *tert.*-butyl malonate and ethyl *tert.*-butyl methylmalonate are obtained in good yield. In general, carbalkoxylation is effected most readily in the case of aryl-substituted acetic esters and appears to be limited to esters carrying two α-hydrogens. If the carbon atom β- with respect to the ester group is tertiary, as in ethyl *tert.*-butylacetate, the yield is extremely low when sodium ethoxide is used;[93] this is not the case, however, if sodium triphenylmethyl is used as the condensing agent.[95] Esters carrying only one α-hydrogen atom do not react with ethyl carbonate, but in such cases carbalkoxylation can be effected by interaction of the sodium enolate of the ester (prepared by using sodium triphenylmethyl) and ethyl chlorocarbonate.[96]

Carbalkoxylation of Ketones.—The condensation of ketones with alkyl carbonates with formation of β-keto-esters has been described by a number of workers. Using acetophenone and ethyl carbonate with sodium ethoxide as condensing agent, L. Claisen [97] obtained a poor yield of ethyl benzoylacetate. O. Schroeter [98] and H. Lux [99] have described the preparation of β-keto-esters from ketones and alkyl carbonates with sodium as condensing agent; a remarkably successful application of this reaction is claimed by N. A. Preobrashenski, M. N. Schtschukina, and R. A. Lapina,[1] who obtained 70—80% yields of tropinonecarboxylic esters by condensation of tropinone with alkyl carbonates in the presence of sodium or potassium. Applying general principles established in the case of the carbalkoxylation of esters, *viz.*, use of a large excess of alkyl carbonate and removal of the alcohol introduced with the sodium ethoxide and that produced by the reaction, V. H. Wallingford, A. H. Homeyer, and D. M. Jones [2] have shown that the carbalkoxylation of ketones by means of alkyl carbonates with sodium ethoxide as condensing agent can be effected in reasonable yield in a large number of cases. Certain limitations to the use of the method are to be noted; ketones which readily polymerise or undergo self-condensation give unsatisfactory yields. Again, in the cases of propiophenone and butyrophenone, the required keto-ester is accompanied by the mixed carbonate of the enolic form of the ketone, $Ar{\cdot}C(O{\cdot}CO_2R){:}CHR'$.

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[88] *Ber.*, 1929, **62**, 1827.

[89] W. L. Nelson and L. H. Cretcher, *J. Amer. Chem. Soc.*, 1928, **50**, 2758.

[90] G. S. Skinner, *ibid.*, 1937, **59**, 322.

[91] *Ibid.*, 1932, **54**, 4319.

[92] *Ibid.*, 1933, **55**, 4597.

[93] V. H. Wallingford, A. H. Homeyer, and D. H. Jones, *ibid.*, 1941, **63**, 2056.

[94] This principle had previously been applied to ester condensation: U.S.P. 1,425,626 (1922), 1,472,324 (1923), 1,805,281 (1931); S. M. McElvain, *J. Amer. Chem. Soc.*, 1929, **51**, 3124; R. R. Briese and S. M. McElvain, *ibid.*, 1933, **55**, 1697.

[95] *J. Amer. Chem. Soc.*, 1942, **64**, 2714.

[96] R. E. Hudson and C. R. Hauser, *ibid.*, 1941, **63**, 3156.

[97] *Ber.*, 1887, **20**, 656.

[98] *Ibid.*, 1916, **49**, 2712.

[99] *Ibid.*, 1929, **62**, 1826.

Carbalkoxylation of Nitriles.—Carbalkoxylation of various aryl acetonitriles by means of alkyl carbonates in the presence of a condensing agent has been described :[3]

$$Ar{\cdot}CH_2{\cdot}CN + CO(OR)_2 \longrightarrow Ar{\cdot}CH(CN){\cdot}CO_2R + ROH$$

F. Adickes and G. Hinderer [4] used alcohol-free sodium ethoxide and enforced the condensation by removal of the alcohol produced during the reaction. In this way they obtained a 63% yield of ethyl α-cyanophenylacetate from phenylacetonitrile and ethyl carbonate. V. H. Wallingford, D. M. Jones, and A. H. Homeyer [5] have shown that the method is not limited to aryl-substituted acetonitriles but is of general applicability; the essential conditions are the use of a large excess of alkyl carbonate and the continuous removal of alcohol from the reaction mixture.

Miscellaneous Reactions.

An analytical method for the estimation of water, alcohols, carboxylic acids and acid anhydrides has been developed by W. M. D. Bryant, J. Mitchell, and D. M. Smith,[6] using the Karl Fischer [7, 8] reagent. This reagent is a solution of iodine, sulphur dioxide and pyridine in methanol; it is extremely sensitive to water, the reagent being its own indicator. Alcohols are esterified with an excess of acetic acid, boron fluoride being used as catalyst; after decomposition of the catalyst, the water produced is estimated by titration with the reagent.

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[1] *Ber.*, 1936, **69**, 1615.

[2] *J. Amer. Chem. Soc.*, 1941, **63**, 2252.

[3] Hessler, *ibid.*, 1940, **32**, 19; W. L. Nelson and L. H. Cretcher, *ibid.*, 1928, **50**, 2758; P. Ruggli, E. Caspar, and B. Hegedüs, *Helv. Chim. Acta*, 1937, **20**, 250; J. B. Niederl, R. T. Roth, and A. A. Plentl, *J. Amer. Chem. Soc.*, 1937, **59**, 1901.

[4] *J. pr. Chem.*, 1938, [ii], **150**, 89.

[5] *J. Amer. Chem. Soc.*, 1942, **64**, 576.

[6] *Ibid.*, 1940, **62**, 1, 4, 608.

[7] *Angew. Chem.*, 1935, **48**, 394.

[8] D. M. Smith, W. M. D. Byrant, and J. Mitchell, *J. Amer. Chem. Soc.*, 1939, **61**, 2409.

Alternative methods for the esterification of sterically hindered acids have been described recently. V. Prelog and M. Plantanides[9] have developed the earlier observation of A. T. Lawson and N. Collie[10] that the tetramethylammonium salts of acids readily decompose on heating to yield the methyl ester of the acid and trimethylamine. With oleanolic and acetyloleanolic acids,[9] 2 : 4 : 6-trimethyl- and 2 : 4 : 6-triethyl-benzoic acids,[11] high yields of the corresponding methyl ester are obtained. M. S. Newman[12] has shown that esterification of a sterically hindered acid is readily achieved by dissolving it in sulphuric acid and pouring the solution into an excess of an alcohol. This attractive method has the advantage of giving a variety of esters in high yield. Equally attractive is the method of hydrolysis of esters of sterically hindered acids described by the same author. The ester is dissolved in sulphuric acid, and the solution poured into water.

A new optically active reagent for carbonyl compounds, *l*-menthyl *N*-aminocarbamate,[13] which is stable and yields crystalline derivatives with a large number of ketones and aldehydes has been described; a successful resolution of *dl*-camphor has been achieved by its means.

A remarkable " carboxylation " of paraffin or *cyclo*paraffin hydrocarbons is described by M. S. Kharasch and H. C. Brown.[14] If, for example, *cyclo*hexane is treated with oxalyl chloride and the solution irradiated or refluxed with a catalytic quantity of benzoyl peroxide, hexahydrobenzoyl chloride is obtained in 65% yield :

$$C_6H_{12} + (COCl)_2 \longrightarrow C_6H_{11}{\cdot}COCl + CO + HCl$$

A chain mechanism is postulated for the reaction. With unsaturated hydrocarbons containing a highly polar double bond, oxalyl chloride reacts in the absence of light and peroxides, as shown by the following examples :

$$Ph{\cdot}CH{:}CH_2 + (COCl)_2 \longrightarrow Ph{\cdot}CH{:}CH{\cdot}COCl + CO + HCl$$
$$CPh_2{:}CH_2 + (COCl)_2 \longrightarrow CPh_2{:}CH{\cdot}COCl + CO + HCl$$

This type of reaction probably proceeds by a polar and not a chain mechanism.[15]

A method for the introduction of cyanoethyl groups into compounds containing an active methylene group has been described by H. A. Bruson.[16] Fluorene reacts with acrylonitrile in the presence of a catalytic amount of trimethylbenzylammonium hydroxide to give (I, $R = CH_2{\cdot}CH_2{\cdot}CN$). In the case of *cyclo*pentadiene, in absence of catalyst, normal 1 : 4-addition of acrylonitrile occurs to give (II); in the presence of the catalyst, however, this reaction is suppressed, and each of the six available hydrogen atoms is replaced to give the hexa-cyanoethyl derivative (III, R = $CH_2 \cdot CH_2 \cdot CN$).

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[9] *Z. physiol. Chem.*, 1936, **244**, 56.

[10] *J.*, 1888, **53**, 631.

[11] R. C. Fuson, J. Corse, and E. C. Horning, *J. Amer. Chem. Soc.*, 1939, **61**, 1920.

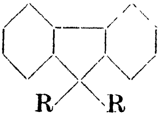
[12] *Ibid.*, 1941, **63**, 2431.

[13] R. B. Woodward, T. P. Kohmann, and G. C. Harris, *ibid.*, g. 121.

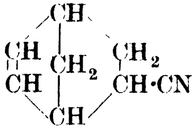
[14] *Ibid.*, 1942, **64**, 329; 1940, **62**, 454.

[15] M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, 1942, **64**, 333.

[16] *Ibid.*, p. 2547.



(I.)



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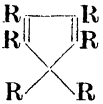

(III.)

The reaction whereby C-methylation of pyrrole derivatives is accomplished by methanolic sodium methoxide [17] has been successfully applied to the indole series by R. H. Cornforth and (Sir) R. Robinson,[18] and the scope of the reaction investigated. The authors show that indole and indole-2-carboxylic acids are converted into 3-alkylindoles when heated with alcoholic sodium alkoxide. Thus skatole is obtained from either indole (71%) or indole-2-carboxylic acid (63%) by heating with methyl-alcoholic sodium methoxide; the reaction succeeds with aliphatic primary alcohols (and the corresponding sodium alkoxide), but alkylation of indole-2-carboxylic acid is not accomplished by secondary alcohols. J. W. Cornforth, (Mrs.) R. H. Cornforth, and (Sir) R. Robinson [19] show that C-methylation of reactive phenols such as β-naphthol and resorcinol can also be accomplished by heating with alcoholic sodium methoxide. The yield is increased if the phenol is first converted into a methylene-bis-derivative or into a *N*-piperidylmethyl derivative. Thus 2 : 2′-dihydroxydi-α-naphthylmethane gives a 75% yield of 1-methyl-2-naphthol.

A simple procedure for the preparation of volatile acid chlorides has been described;[20] it consists in the distillation of the required acid chloride from a mixture of benzoyl chloride and an organic acid.

Although phthalic, maleic and succinic acids, when treated with thionyl chloride, give the corresponding anhydrides [21] (and not the acid chloride), L. P. Kyrides [22] has shown that, when the reaction is carried out in the presence of zinc chloride, the corresponding acid chloride is obtained in good yield (maleic acid giving fumaryl chloride). Developing an earlier observation of van Dorp and van Dorp,[23] it is shown that phthalyl chloride is a valuable reagent for the nearly quantitative conversion of acids and their anhydrides into the corresponding acid chloride.

A valuable method is described by R. Q. Brewster and J. A. Poje,[24] who show that a diazonium salt can be converted into the corresponding

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[17] Fischer-Orth, " Die Chemie des Pyrrols," Leipzig, 1934, I, 33, 287.

[18] *J.*, 1942, 680.

[19] *Ibid.*, p. 682.

[20] H. C. Brown, *J. Amer. Chem. Soc.*, 1938, **60,** 1325.

[21] H. Meyer, *Monatsh.*, 1901, **22,** 437; L. McMaster and F. F. Ahmann, *J. Amer. Chem. Soc.*, 1928, **50,** 145; P. Carré and D. Libermann, *Compt. rend.*, 1934, **199,** 1422.

[22] *J. Amer. Chem. Soc.*, 1937, **59,** 206.

[23] *Rec. Trav. chim.*, 1906, **25,** 96.

[24] *J. Amer. Chem. Soc.*, 1939, **61,** 2418.

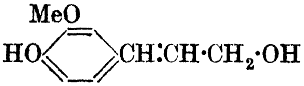
" hydrocarbon " by treatment with alkaline formaldehyde. Yields of 50—80% of the deaminated derivative are obtained from a variety of bases. The method is a valuable supplement to the alcohol method of deamination, since best yields of " hydrocarbon " are obtained in cases where the alcohol method gives poor yields of hydrocarbon and high yields of ether.

F. S. S.

4. The Lignin Problem.

Since the last Report on this subject [1] much work on lignin has appeared and lignin chemistry now rests on sounder foundations than appears from earlier reviews.[2, 3, 4] Since the review by K. Freudenberg,[4] valuable accounts of lignin chemistry have been contributed by H. Hibbert [5, 6] in more than seventy papers in the last twelve years as representing the Canadian, and by H. Erdtman [7] representing the Swedish school.

All the above authors acknowledge the value of the suggestion of P. Klason,[8] that lignin is related to coniferyl alcohol (I), which is present as the glucoside coniferin in all young plant tissue, and in the cambial sap of the spruce, and his later suggestions [9] that coniferyl aldehyde or mixed coniferyl aldehyde-coniferyl alcohol types are fundamental to the lignin structure.



(I.)

Protolignin and Extracted Lignins.—The term protolignin has been suggested [10] to denote the virgin lignins present in plant tissues and it has been shown [11] that these substances are extremely sensitive to acids and alkalis, being transformed into dark amorphous polymers. K. Freudenberg [4] indeed recommends where possible the carrying out of reactions on lignin *in situ* in the ground wood itself, provided the cellulosic constituents either do not react or give easily separable products.

Many attempts have been made to isolate a pure unchanged " native " lignin from various sources. In earlier work the " acid " lignins were much used, involving extraction with concentrated hydrochloric [12] or sulphuric acid,[13] mixtures of hydrochloric and phosphoric acids,[14] and liquid hydrogen fluoride.[15] With the possible exception of the lignin obtained by the last process the products were without doubt highly modified. Much of K. Freudenberg's work has been carried out on "cuproxam" lignin [16] obtained by the extraction of wood meal with dilute sulphuric acid and cuprammonium hydroxide alternately, the latter dissolving the cellulosic portions after decomposition of the supposed lignin–carbohydrate complexes.

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[1] *Ann. Reports*, 1939, **36**, 380.

[2] M. Phillips, *Chem. Reviews*, 1934, **14**, 103.

[3] A. G. Norman, " Biochemistry of Cellulose, the Polyuronides, Lignin, etc." Oxford, 1937.

[4] *Ann. Rev. Biochem.*, 1939, **8**, 88.

[5] *Paper Trade J.*, 1941, **113**, TAPPI Sect. 39.

[6] *Ann. Rev. Biochem.*, 1942, **11**, 183.

[7] *Svensk Papperstidn.*, 1941, **44**, 243.

[8] *Svensk Kem. Tidskr.*, 1897, **9**, 135.

[9] *Ber.*, 1923, **56**, 300; 1930, **63**, 792.

[10] J. König and E. Rump, " Chemie und Structure der Pflanzen-Zell-membran," Berlin, 1914, 85.

[11] A. B. Cramer, M. J. Hunter, and H. Hibbert, *J. Amer. Chem. Soc.*, 1939, **61**, 509.

[12] R. Willstätter and L. Zechmeister, *Ber.*, 1913, **46**, 2401.

Another method of attack, introduced by P. Klason [18] and used by E. Hägglund [19] and others, has been exploited with considerable success by H. Hibbert and his co-workers.[5] This involves extraction with anhydrous alcohols, glycol, glycerol, etc., containing small amounts of hydrogen chloride. The alcohol residues combine with the lignin to give such products as methanol-lignin [20] and glycol-lignin.[21]

B. Holmberg [22] claims that lignins from the most varied botanical sources are essentially of uniform type, but it is clear that lignins from different sources are of different composition, and H. Hibbert and his co-workers have suggested this as a means of differentiating between angiosperms and gymnosperms,[23] since all plants universally recognised as gymnosperms (*e.g.*, spruce) yield lignins which on oxidation with nitrobenzene under alkaline conditions give vanillin only, whereas angiosperms (rye, bamboo, maple, sassafras, aspen, jute) give both vanillin and syringaldehyde.[24] As the result of his oxidation experiments with chlorine dioxide P. B. Sarkar [25] concludes that jute lignin is less highly polymerised than wood lignins.

In all probability lignins are mixtures of compounds of similar type though not of identical composition, and the proportions may vary with the age of the plant and conditions of growth. At present, however, it is necessary to regard lignins extracted from the same sources under the same conditions as essentially identical.

Physical Studies and the Aromatic Nature of Lignin.—If the lignin is carefully prepared, the morphology of the cell is retained. The double refraction observed under the polarising microscope becomes weaker in suspensions in liquids of increasing refractive index and disappears entirely in iodobenzene (n_D 1·62), reappearing with liquids of higher refractive index. The refractive index of lignin is thus estimated to be 1·61 in agreement with its aromatic nature.[26]

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[13] P. Klason, *Cellulosechemie*, 1923, **4**, 81.

[14] K. Freudenberg and H. Urban, *ibid.*, 1926, **7**, 73.

[15] K. Wiechert, *ibid.*, 1940, **18**, 57.

[16] K. Freudenberg, M. Harder, and L. Markert, *Ber.*, 1928, **61**, 1760.

[17] K. Freudenberg, A. Janson, E. Knopf, and A. Haag, *Ber.*, 1936, **69**, 1415.

[18] *Tekn. Tidskr. Avd. Kemi*, 1893, **23**, 55.

[19] E. Hägglund and T. Rosenqvist, *Biochem. Z.*, 1926, **179**, 376.

[20] F. Brauns and H. Hibbert, *Canadian J. Res.*, 1935, **13**, *B*, 28.

[21] K. R. Gray, E. G. King, F. Brauns, and H. Hibbert, *ibid.*, p. 35.

[22] *Svensk Papperstidn.*, 1931, **34**, 215.

[23] E. West, A. S. MacInnes, J. L. McCarthy, and H. Hibbert, *J. Amer. Chem. Soc.*, 1939, **61**, 2556; 1940, **62**, 2803.

[24] R. H. Creighton, J. L. McCarthy, and H. Hibbert, *ibid.*, 1941, **63**, 3049.

[25] *J. Indian Chem. Soc.*, 1935, **12**, 470.

X-Ray analysis reveals no crystalline or pseudocrystalline structure in lignin, its tensile strength is very low, and its mechanical properties are equal in all directions. The thickness of the layers of lignin azobenzene-sulphonic acid was determined to be 20 A., which is taken to indicate a three-dimensional structure.[4]

From the position and intensity of the spectral absorption bands of lignin sulphonic acids, R. O. Herzog [27] characterised it as an aromatic substance with an ultra-violet absorption spectrum similar to that of *iso*eugenol and claimed to show therefrom that the basal unit of lignin is a di- or tri-hydroxyphenol, partly or wholly etherified, having a side chain of about three carbon atoms containing no double bond or carboxyl group conjugated to the benzene ring. Confirmation of these results is supplied by E. Virasoro [28] for quebracho and red willow lignins.

From recent determinations of ultra-violet absorption spectra of lignin,[29] the very persistent absorption band at 2810 A. was related to the assumption that each native lignin building unit contains two pyran rings as proposed by K. Freudenberg.[4] It was also pointed out that the carbonyl group shown by F. E. Brauns [30] to be present in native lignin could be responsible for the band at 2520 A. in the absorption spectrum of the derived phenylhydrazone, and the absence of this band in the lignins examined is held to indicate the enolisation of this group.

J. F. Hechtmann [31] has used the molecular still to attack the problem. At 260°/1 μ a distillate (4%) was obtained which is related to lignin as shown by its absorption spectrum and is held to be partly depolymerised. The residue is considered to be more highly polymerised than the starting material.

From dielectric-constant measurements [32] it is concluded that the molecular weight of lignin is *ca.* 3900 and that normal lignin is fairly homogeneous.

General Analytical Evidence.—Spruce lignins contain C, 65—66%; H, 6%; O, 28—29%; lignins from deciduous woods contain *ca.* 5% less C. The oxygen content of lignin is distributed among different groups, spruce lignin containing OMe, 15—16% and hardwood lignins OMe, 21—22%. Hydroxyl groups occur to the extent of *ca.* 9% in spruce lignin, of which

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[26] K. Freudenberg, H. Zucker, and W. Dürr, *Ber.*, 1929, **62**, 1814.

[27] R. O. Herzog and H. Hilmer, *Ber.*, 1927, **60**, 365; 1931, **64**, 1288.

[28] E. Virasoro, *Anal. Asoc. Quim. Argentina*, 1942, **30**, 54.

[29] R. E. Glading, *Paper Trade J.*, 1940, **111**, TAPPI Sect., 288.

[30] *J. Amer. Chem. Soc.*, 1939, **61**, 2120.

[31] *Paper Trade J.*, 1942, **114**, TAPPI Sect., 259.

[32] W. P. Conner, *J. Chem. Physics*, 1941, **9**, 591.

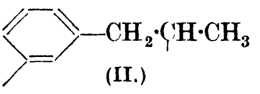
6—7% are secondary and the remainder tertiary.[33] K. Freudenberg *et al.*[34] claim a proportion of methylenedioxy-residues (4%), but H. Hibbert[35] makes other suggestions as to the probable source of the formaldehyde on which this conclusion is based and points out[5] that piperonyl derivatives have never been isolated by the degradation of lignin and that but a minute yield (0·03%) of formaldehyde results from sassafras lignin, although it would be natural to expect methylenedioxy-groups to be present in this case, since the plant is the source of safrole.[36]

The remainder of the oxygen, *ca.* 7·5%, is considered to be ether oxygen. Estimation of the acetic acid liberated by oxidation with chromic acid[37] shows that at least 2·7% of methyl groups bound to carbon are present, and, since this is approximately equal to the amount of tertiary hydroxyl, the presence of the >CMe·OH group is inferred. Free phenolic groups appear to exist in small amount approximately equivalent to the tertiary hydroxyl group content.

Evidence of the aromatic nature of lignin is provided by the formation of mercury substitution products by treatment with mercuric acetate,[38] the mercury being replaceable by iodine. Bromination[39] and nitration[40] show that up to two hydrogen atoms in each aromatic nucleus can be substituted.

The Views of Karl Freudenberg.

Freudenberg[4] points out that, if all the oxygen atoms, methoxyl, and methylenedioxy-residues in lignin are replaced by hydrogen, a hydrocarbon is obtained best expressed by C_9H_{10}, *i.e.*, phenylpropane minus two hydrogen atoms (II), and suggests that this is the fundamental type-unit of the lignin molecule, the central idea being that "lignin is composed of similar units which unite with each other like the amino-acids in proteins or the monoses in polysaccharides. We assume that the units are connected through an ether linkage between phenolic hydroxyl and the carbinol group in the side chain."



(II.)

Starting with guaiacylglycerol and acetylguaiacylcarbinol, this worker visualises condensation to such products as (III) and (IV) and an extension of this principle to form chains of such units, (V) and (VI).

No phenylpropane derivatives, however, have been isolated by this worker, his conclusions being based on C_6–C_1 fragments. Credit for the experimental confirmation of this theory, without which these speculations are of little value, must be given to Harold Hibbert and his school (p. 150

[33] K. Freudenberg, F. Sohn, and A. Janson, *Annalen*, 1935, **518**, 62.

[34] K. Freudenberg, F. Klink, E. Flickinger, and E. Sobek, *Ber.*, 1939, **72**, 217.

[35] M. J. Hunter, G. F. Wright, and H. Hibbert, *Ber.*, 1938, **71**, 734.

[36] M. J. Hunter and H. Hibbert, *J. Amer. Chem. Soc.*, 1939, **61**, 2196.

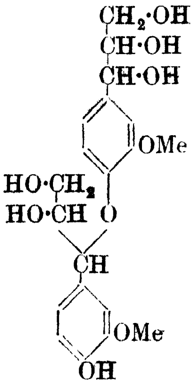
[37] K. Freudenberg and F. Sohns, *Ber.*, 1933, **66**, 262.

[38] K. Freudenberg and H. F. Müller, *Ber.*, 1938, **71**, 2500.

[39] K. Freudenberg, W. Beltz, and C. Niemann, *Ber.*, 1939, **72**, 1554.

[40] K. Freudenberg and W. Dürr, *Ber.*, 1930, **63**, 2713.

et seq.). The assumption is also made that condensation to form chroman (VII) or furan (VIII) rings may occur, although the uncondensed ether systems may be present also. The main features of these formulæ may be represented by (IX) and (X).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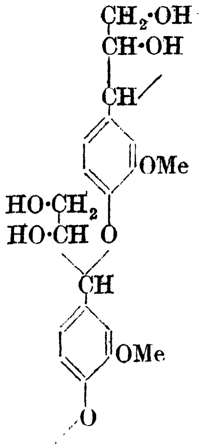
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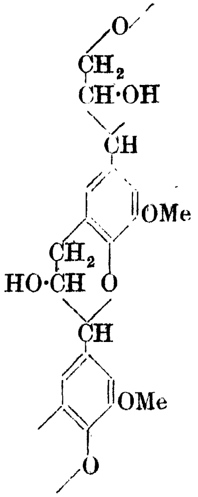
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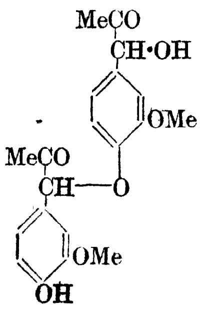
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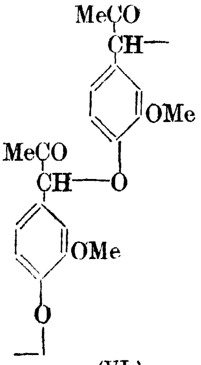
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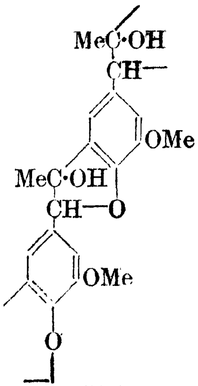
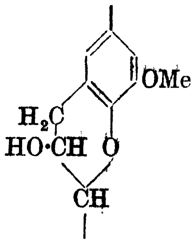
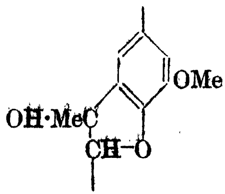
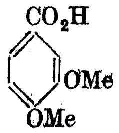

(VIII.)


(IX.)

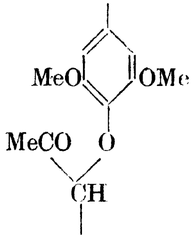

(X.)

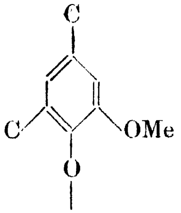

(XI.)

Freudenberg considers that the few end groups in lignin are present in the form shown by (III) and (IV), because methylation, followed by oxidation, yields only a relatively small amount of veratric acid (XI). He states also that the groups which split off formaldehyde on treatment with acid are intermediate members within the chains, but admits that there is as yet no proof of this.

From the isolation of the pyrogallol component of the oxidation products of beech lignin as the symmetrical dimethyl ether, it is concluded that units like (XII) can occur, and the same is assumed to be true for the pyrogallol component of spruce lignin.

(XII.)





(XIII.)

To sum up, Freudenberg considers that five out of eight units in spruce lignin belong to types like (IX) or (X), two units contain methylenedioxy-groups and one is of the pyrogallol type (XII), the average molecular weight per unit being 185. Condensation to form two- or three-dimensional units is also envisaged.[4]

On the basis of the isolation of vanillin-5-carboxylic acid from spruce lignin, the above views have been somewhat modified[41] and it is now stated that at least half of the basal units in spruce are represented by (XIII).

The experimental evidence on which the above theories rest is summarised below. Potash fusion of spruce lignin yields protocatechuic acid (10%), isolated as veratric acid (XI), this yield being comparable with that obtained from eugenol or polymerised coniferyl alcohol on similar treatment,[33] and from beech lignin, gallic acid, as trimethylgallic acid, and protocatechuic acid (3—3·5%) are obtained.[17, 42] If spruce meal is treated with diazomethane, and the product oxidised with permanganate, veratric acid (4%, based on the lignin content) is obtained,[43] from which it may be concluded that every sixteenth unit, on the average, possesses a free guaiacyl end group and that lignin in wood contains approximately 0·6% of free phenolic groups. The yield of veratric acid from isolated spruce lignins is lower (1—2%), so most of the veratric acid may originate from lignin precursors of low molecular weight.

The main evidence adduced in favour of the above theoretical schemes is secured by treatment of spruce wood-meal with diazomethane, followed by potassium hydroxide solution (70%) at 165—170°, methylation with methyl sulphate, and oxidation with permanganate to yield veratric acid (XI) (20—21%), *iso*hemipinic acid (XIV) (6—12%), dehydroveratric acid (XV) (2—3%), and trimethylgallic acid (XVI) (in traces).[44] Lower values are obtained for isolated lignins.[17, 43]

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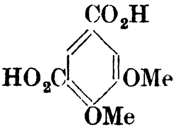
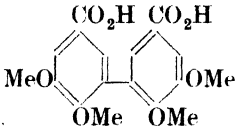
[41] K. Freudenberg and F. Klink, *Ber.*, 1940, **73**, 1369.

[42] K. Freudenberg and H. F. Müller, *Ber.*, 1938, **71**, 1821.

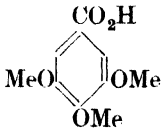
[43] K. Freudenberg, M. Meister, and E. Flickinger, *Ber.*, 1937, **70**, 500.



(XIV.)

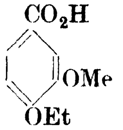


(XV.)

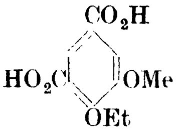


(XVI.)

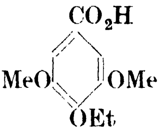
By substituting ethylation for methylation, evidence was obtained, by the isolation of (XVII) and (XVIII), albeit in poor yield, that the ether bonds which open are as indicated and are here occupied by ethyl groups.



(XVII.)

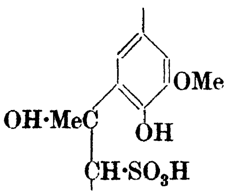


(XVIII.)



(XIX.)

By examining the yields recoverable by treating (XI), (XIV), (XV), (XVI), and piperonylic acid with the above reagents,[34] and applying correction factors to the yields obtained from spruce lignin, the true yield [44] of (XIV) is calculated to be 80% and of (XI) and (XV) combined, 32%. The high correction factor (× 9) for (XIV) is unfortunate, as is also the fact that this method gives no practical evidence for the presence of methylenedioxy-groups, the presence of which is denied by H. Hibbert.[35] H. Erdtman [7] considers that the drastic alkaline conditions introduce a very uncertain factor and that a large portion of the isolated (XIV) may be formed by secondary condensation reactions between aromatic nuclei and side chains. On account of the difficulty of separating (XVI) similar experiments with beechwood lignin are less satisfactory, the corrected yields being (XI) 7%, (XIV) 13·5%, and (XVI) 13%. By the ethylation technique beech lignin gives, in addition to the ethyl ether of vanillic acid (XVII), the ethyl ether of syringic acid (XIX) in harmony with the fact that symmetrical dimethylpyrogallol derivatives are found in the distillation products of beech lignin.



(XX.)

Freudenberg [4] supposes that the formation of lignin sulphonic acids by reaction with sulphites is due to the rupture of ether linkages (X) in every third unit with the appearance of new phenolic residues (XX), since a higher yield of (XI) is obtained by methylation, followed by oxidation, than from lignin itself. Methylenedioxy-groups appear to be largely eliminated by the sulphite cooking process.

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[44] K. Freudenberg, K. Engler, E. Flickinger, E. Sobek, and F. Klink, *Ber.*, 1938, **71**, 1810.

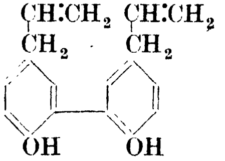
A similar explanation is also applied to B. Holmberg's reaction[4] with thioglycollic acid, $S{\cdot}CH_2{\cdot}CO_2H$ replacing SO_3H in (XX).

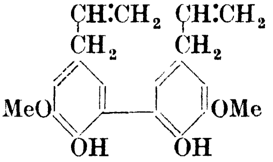
The Views of Holger Erdtman.

Erdtman[7] points out that structures such as (V) and (VI) would be expected to show special reactivity in the CH residue *para* to the methoxyl group and considers that the probable direction of the condensation should involve the hydroxyl group of the side chain with an adjacent molecule in the *p*-position to the methoxyl group. Furthermore, the transformation of (V) into (VII) appears improbable, since condensations of this type generally require alcohols having hydroxyl groups on carbon atoms directly attached to the benzene nucleus, *e.g.*, benzyl alcohol.

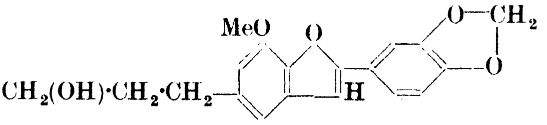
Erdtman also draws attention to the mode of attachment of naturally occurring dimeric forms of phenylpropane units in substances such as magnolol[45] (XXI), dehydroeugenol[46] (XXII), and egonol[47] (XXIII).

(XXI.)



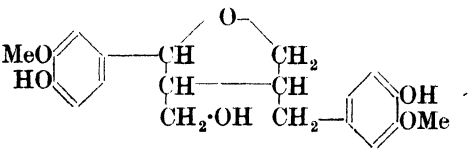


(XXII.)

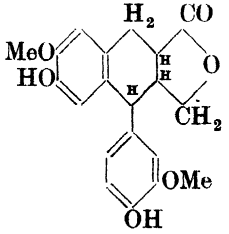


(XXIII.)

The lignans, products of great importance in wood chemistry, such as pinoresinol,[48] lariciresinol[49] (XXIV), and conidendrin[50] (XXV) always have the *middle* carbon atom in the side chain as the connecting atom, as in (VIII) but not as in the Freudenberg formula (VII).



(XXIV.)



(XXV.)

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[45] Y. Sugii, *Chem. Zentr.*, 1930, II, 253.

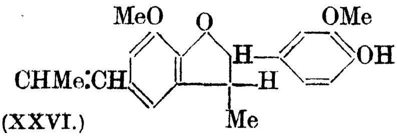
[46] H. Cousin and H. Hérissey, *Compt. rend.*, 1937, **146**, 1413; H. Erdtman, *Biochem. Z.*, 1933, **258**, 172.

[47] S. Kawai and N. Sujiyama, *Ber.*, 1939, **72**, 369.

[48] H. Erdtman, *Annalen*, 1933, **503**, 283.

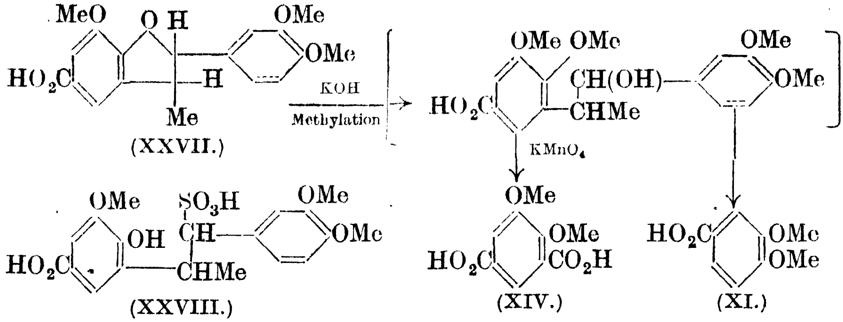
[49] R. D. Haworth and W. J. Kelly, *J.*, 1937, 384; R. D. Haworth and D. Woodcock, *J.*, 1939, 1054.

[50] R. D. Haworth, T. Richardson, and G. Sheldrick, *J.*, 1935, 1576.



(XXVI.)

In 1933 Erdtman,[46] on the basis of the production of dehydrodi*iso*eugenol (XXVI) by the action of ferric chloride on, or the enzymatic dehydrogenation of *iso*eugenol, suggested that lignin might be a high-molecular-weight dehydrogenation product of phenylpropane derivatives and K. Freudenberg *et al.*[43] have used (XXVI) as a type model for many lignin reactions. By methylation of (XXVI), followed by cautious oxidation, Erdtman[46] obtained an acid (XXVII), from which Freudenberg and his co-workers obtained (XI) (21% instead of 53%) and (XIV) (5% instead of 66%), a result not very different from that obtained for lignin itself under similar conditions [(XI), 14%; (XIV) 4%]. Under the conditions of the sulphite treatment[51] an acid (XXVIII) was obtained which gave on methylation and oxidation (XI) (17% instead of 39%) and (XIV) (4% instead of 40%); compare ligninsulphonic acid, which gives (XI) 3% and (XIV) 3·8%.



Similar analogies between (XXVII) and lignin are shown in its reactions with thioglycollic acid, on methanolysis, and with hydrazine.[4]

The Views of Harold Hibbert.

Much of the value of the work of Hibbert and his school lies in the cautious way in which he has interpreted his results, the full value of which is now clearly discernible. The development of the alcoholysis method for the isolation of lignin[52] yielded much useful information. A more fruitful field has proved to be his studies of the action of alkali on the ligninsulphonic acids. Spruce ligninsulphonic acid gave vanillin (6—7%),[53] and this is not only a commercial outlet for waste sulphite liquor but shows the importance of the guaiacyl nucleus in the lignin molecule. Soon afterwards small amounts of acetovanillone (XXIX)[54] and guaiacol[55, 56] were isolated together with the vanillin. Oak and maple ligninsulphonic acids gave, in addition, syringaldehyde [57] (XXX), acetosyringone [58] (XXXI), and 1 : 3-*O*-dimethylpyrogallol [56] (XXXII).

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[51] K. Freudenberg, *Papierfabrikant*, 1938, **36**, 34.

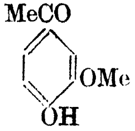
[52] H. Hibbert and H. J. Rowley, *Canadian J. Res.*, 1930, **2**, 357 *et seq.*

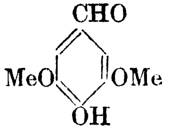
[53] G. H. Tomlinson and H. Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 345.

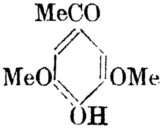
[54] I. H. Buckland, G. H. Tomlinson, and H. Hibbert, *ibid.*, 1937, **59**, 597.

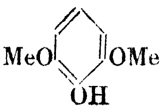
[55] F. Leger and H. Hibbert, *Canadian J. Res.*, 1938, **16**, *B*, 68.

[56] *Idem, ibid.*, p. 151; *J. Amer. Chem. Soc.*, 1938, **60**, 565.


(XXIX.)

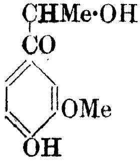

(XXX.)

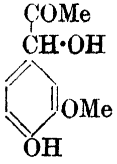

(XXXI.)

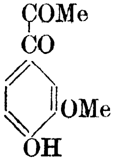

(XXXII.)

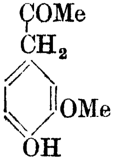
The isolation of (XXIX) and (XXXI) indicated for the first time the existence of side chains of two carbon atoms in at least some of the lignin building stones. K. Freudenberg *et al.*[58] later obtained, by the action of nitrobenzene and alkali on spruce ligninsulphonic acid, a higher yield of vanillin (25%): this was confirmed [59] and the same technique applied to aspen and maple woods gave a mixture of vanillin and syringic aldehyde (40—45%).[59] These results prove beyond doubt the aromatic character of lignin and dispose of the theory of its carbohydrate nature.[60] The failure to isolate piperonyl derivatives, as already mentioned, throws doubt on K. Freudenberg's view [4] that spruce lignin contains 25% of these nuclei.

The most important advance in lignin chemistry has been made as the result of Hibbert's experiments on the treatment of various plant materials, such as maple wood, with ethanolic hydrogen chloride (2%); ethoxyl-containing ethanol-lignins of high molecular weight (*ca.* 60% of the Klason lignin content), together with soluble distillable fractions (30%) of low molecular weight,[61] were thus isolated. The products so far identified (*ca.* 13%) in this mixture are: for spruce, vanillin, β-hydroxy-α-(4-hydroxy-3-methoxyphenyl)-α-propanone (XXXIII),[62] α-hydroxy-α-(4-hydroxy-3-methoxyphenyl)-β-propanone (XXXIV),[64] α-(4-hydroxy-3-methoxyphenyl)-αβ-propanedione (XXXV),[63] and α-(4-hydroxy-3-methoxyphenyl)-β-propanone (XXXVI); [64] for maple wood, both these and the corresponding syringyl


(XXXIII.)


(XXXIV.)


(XXXV.)


(XXXVI.)

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[57] A. Bell, W. L. Hawkins, G. F. Wright, and H. Hibbert, *ibid.*, 1937, **59**, 598.

[58] K. Freudenberg, W. Lautsch, and K. Engler, *Ber.*, 1940, **73**, 167.

[59] R. H. J. Creighton, J. L. McCarthy, and H. Hibbert, *J. Amer. Chem. Soc.*, 1941, **63**, 312.

[60] R. S. Hilpert, *Cellulosechemie*, 1936, **17**, 25.

[61] L. Brickman, J. J. Pyle, J. L. McCarthy, and H. Hibbert, *J. Amer. Chem. Soc.*, 1939, **61**, 868.

[62] A. S. MacInnes, E. West, J. L. McCarthy, and H. Hibbert, *ibid.*, 1940, **62**, 2803.

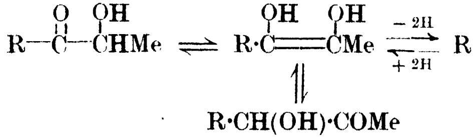
[63] L. Brickman, W. L. Hawkins, and H. Hibbert, *ibid.*, p. 2149.

[64] H. Hibbert, private communication.

derivatives.[64, 65, 66] The products (XXXIII) and (XXXIV) and their syringyl analogues were isolated in the form of their ethyl ethers as a result of the ethanolysis.

The importance of the characterisation of these derivatives is that all are derivatives of phenylpropane and thus fit in with the theoretical speculations of K. Freudenberg. It appears that there is a positive relationship between lignin and the above ethanolysis products, for ethanol-lignin on treatment in this way yields a proportion of these simple products.[67] At the same time, however, irreversible polymerisation reactions proceed, thus limiting the yield of distillable oils.

H. Hibbert points out [4] the similarity between the structure of the units formed by the ethanolysis of lignin and the ene-diol oxidase system of A. Szent-Györgyi.[68] The hydroxy-compounds corresponding to (XXXVI) and its syringyl analogue are benzoins, compounds which are well known to resinify in the presence of mineral acid and also undergo ene-diol dismut-



$$\begin{tikzcd}R\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{OH}{\overset{|}{C}}HMe \arrow[r, phantom, "\rightleftharpoons"] & R\cdot\overset{OH}{\overset{|}{C}}=\!=\overset{OH}{\overset{|}{C}}Me \arrow[r, "-2H"', shift left] \arrow[d, shift left] & R\cdot CO\cdot COMe \arrow[l, "+2H", shift left] \\ & R\cdot CH(OH)\cdot COMe \arrow[u, shift left] & \end{tikzcd}$$

R = guaiacyl or syringyl

ation, and Hibbert considers that the ene-diols may act as reductants of ene-diol-1 : 2-diketone systems, the oxidants being the vanilloyl (XXXV) and syringoyl methyl ketones isolated above. The suggestion is made that, analogous to the animal respiratory catalyst system of A. Szent-Györgyi (C_4 system), there exists a system of plant respiratory catalysts (C_6–C_3 system), made up of mono- and di-hydroxyconiferyl alcohols in equilibrium with their keto-forms, in which coniferyl or syringyl alcohol appears as the analogue of fumaric acid in the C_4 systems, and that lignin is essentially a product derived from these plant respiratory catalysts. In this connection the changes

$$\begin{tikzcd}R\cdot CH_2\cdot CO\cdot CH_2\cdot OH \arrow[r, phantom, "\rightleftharpoons"] & R\cdot CH{:}C(OH)\cdot CH_2\cdot OH \arrow[r, phantom, "\rightleftharpoons"] & R\cdot CH(OH)\cdot C(OH){:}CH_2 \arrow[d, shift left] \\ R\cdot CO\cdot CH(OH)\cdot CH_3 \arrow[r, phantom, "\rightleftharpoons"] & R\cdot C(OH){:}C(OH)\cdot CH_3 \arrow[r, phantom, "\rightleftharpoons"] & R\cdot CH(OH)\cdot CO\cdot CH_3 \arrow[u, shift left]\end{tikzcd}$$

and $$R\cdot CH(OH)\cdot CO\cdot CH_3 \underset{-2H}{\overset{+2H}{\rightleftharpoons}} R\cdot CO\cdot CO\cdot CH_3$$

(R = guaiacyl) have recently been realised experimentally *in vitro* by H. Hibbert and his co-workers.[64]

E. E. Harris, J. D'Ianni, and H. Adkins [69] studied the catalytic hydrogenation of a methanol aspen lignin and isolated 4-*n*-propyl*cyclo*hexanol

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[65] M. Kulka, W. L. Hawkins, and H. Hibbert, *J. Amer. Chem. Soc.*, 1941, **63**, 2371.

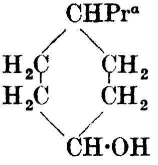
[66] M. J. Hunter, A. B. Cramer, and H. Hibbert, *ibid.*, 1939, **61**, 516.

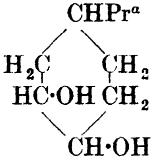
[67] W. B. Hewson, J. L. McCarthy, and H. Hibbert, *ibid.*, 1941, **63**, 3061.

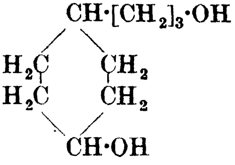
[68] *Ber.*, 1939, **72**, 53 A.

[69] *J. Amer. Chem. Soc.*, 1938, **60**, 1467.

(XXXVII), 4-*n*-propyl*cyclo*hexane-1 : 2-diol (XXXVIII), and γ-(4-hydroxy*cyclo*hexyl)propanol (XXXIX), all of which were synthesised.[69, 70] H. Hibbert and his co-workers,[71] by the hydrogenation of spruce and maplewood, isolated (XXXVII) and (XXXIX) in yields of 19·5% and 5·8% respectively. A re-investigation showed the (XXXVII) fraction to be a mixture of that substance with γ-*cyclo*hexylpropanol in the ratio of 1 : 1.[72]


(XXXVII.)


(XXXVIII.)


(XXXIX.)

Y. Hatihama *et al.*,[73] using less active catalysts, hydrogenated hydrochloric acid lignin and obtained *n*-propylguaiacol, and similar results have been reported by K. Freudenberg and his co-workers.[74]

These hydrogenation results are explained by the rupture of the ether linkages and lend further support to the phenylpropane theory of lignin structure. That oxygen is attached to the terminal carbon atom of the propyl side chain in protolignin is shown by the fact that about half of the propyl*cyclo*hexane derivatives from wood [71] and certain lignins [69, 75] have oxygen in that position (XXXIX). A comparison of the hydrogenation of maple ethanol-lignin and maple wood shows that a terminal primary alcohol or methylene ether group is present in the protolignin because of the higher yield of (XXXIX) obtained from the latter.[5] The examination of hydrogenation products of fractions of a maple ethanol-lignin [75] shows that " for a given series of such fractions, there is a parallel between increasing solubility and susceptibility to depolymerisation into simple propylphenol units, and the increasing yield of the water-insoluble propyl*cyclo*hexanol degradation products." The conclusion is drawn that those readily soluble lignin units which are easily depolymerised by ethanolysis and hydrogenolysis contain large numbers of C–O–C bonds, whereas in the lignin fractions which exhibit these properties to a less degree C–C–C bonds are more numerous. A somewhat similar conclusion is drawn by H. Adkins and his co-workers,[76, 77] who show that " soda lignin " from mixed hardwoods contains one oxygen per 13·6 carbon atoms and methanol-lignin (from fresh aspen) one oxygen atom for six carbon atoms and conclude that in the treatment of lignin with soda further cyclisation has occurred.

[70] E. Bowden and H. Adkins, *J. Amer. Chem. Soc.*, 1940, **62**, 2422.

[71] H. P. Godard, J. L. McCarthy, and H. Hibbert, *ibid.*, 1941, **63**, 3061.

[72] J. R. Bower and H. Hibbert, unpublished results.

[73] *J. Soc. Chem. Ind. Japan*, 1940, Suppl. **43**, 127.

[74] *Ber.*, 1941, **74**, 171.

[75] L. M. Cooke, J. L. McCarthy, and H. Hibbert, *J. Amer. Chem. Soc.*, 1941, **63**, 3056.

[76] E. E. Harris and H. Adkins, *Paper Trade J.*, 1938, **107**, TAPPI Sect., 38.

[77] H. Adkins, R. L. Frank, and E. S. Bloom, *J. Amer. Chem. Soc.*, 1941, **63**, 3041.

The same also applies to alkali and sulphuric acid lignins, which appear to be more complex than alcohol lignins or protolignin.

Further light has been thrown on the nature of the terminal group in the protolignin building unit by oxidation with chromic acid and estimation of the liberated acetic acid,[64] spruce and maple wood, various ethanol-lignins, and thirteen substances, such as vanilloyl methyl ketone, thought to be closely related to the lignin progenitors, being used. The results show the absence of terminal methyl groups in the three carbon side chains attached to the aromatic nuclei in the " native lignin " present in spruce and maple wood, and in the various insoluble maple ethanol-lignins. The amount of acetic acid obtained from the spruce ethanol-lignin is equivalent to one terminal methyl group in four or five phenylpropane units, which is the same as that obtained for a spruce " cuproxam " lignin.[37] The amount of acetic acid liberated from ethanol-lignins depolymerised by further ethanolysis was doubled, showing that terminal methyl groups are exposed by this treatment.

Taking a broad view of all the results and views expressed above, the suggestion of R. D. Haworth [78] that lignin represents the polyterpene of the C_6–C_3 metabolism and his further suggestion [79] " that the wide distribution of the *n*-propylbenzenes and the lignans in unrelated plant families is a strong indication of their association with a general metabolic process, and in spite of the inconclusive state of knowledge concerning the constitution of lignin, the relationships are sufficiently striking to indicate that the *n*-propylbenzenes and the lignans are connected with the lignification process " are clearly justified.

The Nature of the Union between Lignin and Other Plant Constituents.

Since the extent to which polymerisation of the protolignin takes place during extraction is unknown, the problem of deciding whether the lignin precursors or protolignin are attached to the carbohydrates of wood by glycosidic or ether linkages is difficult to solve. The fact that the C_6–C_3 units, whatever they may be, exist almost certainly in the early stages of growth as simple glycosides, *e.g.*, coniferin, does not necessarily mean that the carbohydrate–lignin complex which is generally assumed to exist contains glycosidic linkages also.

A. J. Bailey [80] has studied the extraction of butanol-lignin by butanol–water and butanol–water–alkali and has shown that all the lignin of aspen can be removed at 160° in 7 hours with aqueous butanol previously buffered to neutrality. Furthermore, the extraction of 93% of the lignin content of poplar has been achieved [81] by heating with a concentrated solution of sodium cymenesulphonate at 105° for 30 hours, and these experiments seem to point to a relatively weak carbohydrate–lignin union, if indeed any exists in these cases. The enzymic degradation experiments of T. Ploetz [82] seem to show that some form of combination does exist and A. G. Norman [3] holds the view that hemicellulose–lignin complexes exist in wood.

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[78] *Nature*, 1941, **147**, 255.

[79] R. D. Haworth, Tilden Lecture, *J.*, 1942, 448.

[80] *Paper Trade J.*, 1940, **110**, No. 2, 29; No. 6, 27; No. 7, 27; **111**, No. 9, 86.

[81] Felipetz, Ph.D. Thesis, Columbia University, 1937.

H. Hibbert and co-workers,[83] from their experiments on the hydrolysis of glycosides such as acetovanillone-β-cellobioside and the corresponding glucoside and xyloside, α-hydroxypropiovanillone- and α-hydroxysyringone-β-*d*-xylosides and α-hydroxypropioveratrone-β-*d*-glucoside, conclude that the aliphatic type of glycoside linkage as found in the last is unlikely and that a phenolic glycoside linkage " is a plausible type for the lignin–carbohydrate linkage of wood if such exists." Much further work remains to be carried out before this problem can be decided.

E. G. V. P.

5. POLYCYCLIC AROMATIC COMPOUNDS.

The polycyclic aromatic hydrocarbons were last reviewed in a general article in these Reports [1] in 1933; since then a large volume of material has been published dealing with work in this field. Reports have already appeared on the rubenes [2] and on naturally occurring polycyclic quinones,[3] and the scope of the present article will be limited by omitting references to these and to polycyclic hydrocarbons resulting from the dehydrogenation of natural products. Only compounds containing more than two condensed rings are discussed, and, as the chemistry of dyes and their intermediates is regularly reviewed in the *Annual Reports of the Progress of Applied Chemistry*, the polycyclic compounds which come in this category receive little attention. Much of the recent progress has been concerned with the development of synthetic methods. Methods which are directed primarily to the production of hydroaromatic structures have already been reviewed.[4, 5] The ease with which aromatic structures may be obtained from the hydroaromatic compounds by dehydrogenation often renders these methods very suitable for the production of purely aromatic polycyclic compounds. Even with the limitations imposed by the omission or curtailment of these sections of the subject the field for review remains too large for adequate treatment, and the selection of topics within this field has been determined largely by the personal interests of the Reporter.

Hydrocarbons of Coal Tar.

At the time of the appearance of A. E. Everest's book [6] it might reasonably have been assumed that knowledge of the constituents of coal tar was approaching finality. That this was not so has been shown by the large number of polycyclic aromatic compounds isolated from the higher-boiling fractions of coal tar during recent years. For the most part these were already known as synthetic compounds, so their identification has presented little difficulty. Much of this new work on high-boiling tar fractions has been carried out by O. Kruber, who has recently summarised the results.[7] Thus, 7 of the 10 possible dimethylnaphthalenes have been isolated [8] as well as 2 : 3 : 6- and 1 : 3 : 7-trimethylnaphthalene.[9] Polycyclic hydrocarbons and their derivatives shown to be present in coal tar include 1-, 3-, and 9-methylphenanthrene,[10] 2-hydroxyphenanthrene,[11] 4 : 5-methylenephenanthrene,* [12] triphenylene (LXXVII),[13] 2- and 3-methylfluorene,[14] 2-hydroxyfluorene,[15] 1 : 2- and 2 : 3-benzfluorene,[16] cyanofluorenes [10] and 1 : 2-benzanthracene.[17, 18] The two theoretically possible benzpyrenes also have been isolated from coal tar [17] and one of these, the 3 : 4-compound † (IV), was found to be a very potent cancer-producing hydrocarbon. According to an estimate quoted by Kruber,[7] 132 kg. of ordinary coal tar pitch contains 1 g. of carcinogenic 3 : 4-benzpyrene. A much higher value is given by A. Winterstein,[19] who used the chromatographic adsorption technique for the isolation of 3 : 4-benzpyrene.[20] Winterstein obtained 2·5 g. of almost pure benzpyrene from 50 kg. of tar, which contained 3 kg. of material boiling above 450°. Chromatography has also been used for the separation of mixtures of polycyclic aromatic hydrocarbons [21] and for the isolation and purification of other higher coal tar hydrocarbons.[22]

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[82] *Ber.*, 1940, **73**, 790.

[83] J. H. Fisher, W. L. Hawkins, and H. Hibbert, *J. Amer. Chem. Soc.*, 1941, **63**, 3031.

[1] G. A. R. Kon, *Ann. Reports*, 1932, **29**, 163.

[2] R. D. Haworth, *ibid.*, 1937, **34**, 389.

[3] A. R. Todd, *ibid.*, 1941, **38**, 205.

[4] R. P. Linstead, *ibid.*, 1936, **33**, 312.

[5] H. D. Springall, *ibid.*, 1939, **36**, 286.

[6] " The Higher Coal Tar Hydrocarbons," London, 1927.

3 : 4-Benzyprene appears to be a feebly coloured (yellow) hydrocarbon. Two deep orange hydrocarbons have been isolated from coal tar. These are naphthacene (2 : 3-benzanthracene) (XIII) [20, 22] and perylene (XLV).[17] The former is the " chrysogen " which imparts the yellow colour to incompletely purified coal-tar anthracene.[23] In addition to the polycyclic hydrocarbons and their derivatives a considerable series of heterocyclic compounds

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[7] *Angew. Chem.*, 1940, **53**, 69.

[8] Compare O. Kruber and A. Marx, *Ber.*, 1939, **72**, 1970.

[9] O. Kruber, *ibid.*, p. 1972.

[10] O. Kruber and A. Marx, *Ber.*, 1938, **71**, 2478.

[11] O. Kruber, *Ber.*, 1936, **69**, 246.

[12] *Idem, Ber.*, 1934, **67**, 1000.

[13] H. Kaffer, *Ber.*, 1935, **68**, 1812.

[14] O. Kruber, *Ber.*, 1932, **65**, 1382.

[15] *Idem, Ber.*, 1936, **69**, 107.

[16] *Idem, Ber.*, 1937, **70**, 1556.

[17] J. W. Cook, C. L. Hewett, and I. Hieger, *J.*, 1933, 396.

[18] O. Kruber, *Ber.*, 1941, **74**, 1688.

[19] *Festschrift Emil Barell*, p. 320; Basle, 1936.

[20] A. Winterstein and K. Schön, *Naturwiss.*, 1934, **22**, 237.

[21] *Idem, Z. physiol. Chem.*, 1934, **230**, 146.

[22] A. Winterstein, K. Schön, and H. Vetter, *ibid*, p. 158.

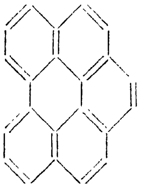
[23] Compare J. W. Cook *et al.*, *Proc. Roy. Soc.*, 1932, *B*, **111**, 469.

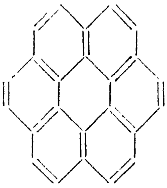
* This tetracyclic hydrocarbon was subsequently synthesised by W. E. Bachmann and J. C. Sheehan (*J. Amer. Chem. Soc.*, 1941, **63**, 204).

† *Note on Nomenclature.*—Throughout this Report the Richter system of numbering is usually employed where numbering is necessary (but see p. 158). In the American literature other systems, including the Patterson system, are often used. In this connection attention is called to " The Ring Index " by A. M. Patterson and L. T. Capell (New York, 1940).

(with cyclic oxygen, nitrogen or sulphur) has been isolated in recent years from the higher-boiling fractions of coal tar.[24] Phenanthrene has been isolated from Roumanian petroleum by I. Gavăt and I. Irimescu.[25]

An interesting new source of higher aromatic hydrocarbons has been found in the products of destructive catalytic hydrogenation of coal or tar oils or pitch.[26] The crude products are submitted to dehydrogenation and to selective extraction with solvents, and in this way such coal tar hydrocarbons as pyrene (XXVIII) (and its homologues), fluorene (XXVI), and chrysene (CXXXIV) may be obtained. Pyrene and chrysene appear to be particularly abundant, and yields of pyrene have been claimed amounting to 1% on the coal used or 8% on the total heavy oil. In view of the difficulty of isolating these two hydrocarbons in quantity from coal tar [27] this new source should offer considerable possibilities of commercial development. From the hydrogenated oils have also been isolated complex hydrocarbons not so far found in coal tar, namely, 1 : 12-benzperylene (I) and coronene (II).[28]


(I.)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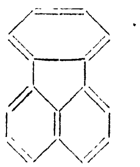
(III.)

Ultra-violet absorption data of coronene are given by J. W. Patterson,[29] and a new synthesis from 7-methyl-1-tetralone has been described.[30]

Another new source of polycyclic aromatic hydrocarbons has been found in the products of thermal decomposition of natural gas. Methane, its chief constituent, is largely decomposed to carbon black and hydrogen when passed over strongly heated refractory material. By cooling the emitted gas, a waxy solid is obtained, and from this A. W. Campbell, N. H. Cromwell, and J. J. Hager [31] isolated acenaphthylene and pyrene. By solvent extraction of the carbon black prepared by this process, J. Rehner [32] obtained fluoranthene (III) (3·5 g. from 5 kg. of carbon black).

Carcinogenic Hydrocarbons.

The cancer-producing action of many of the polycyclic aromatic hydrocarbons has caused much attention to be given to the synthesis and chemistry of compounds of this class. Comprehensive reviews have been published dealing with the structural relationships of the carcinogenic compounds and their biological effects.[33] These carcinogenic hydrocarbons fall into two main groups. The major group is related to 1 : 2-benzanthracene, and a second group is related to 3 : 4-benzphenanthrene (cf. CXX). It is possible to state in general terms the nature and positions of substitution likely to lead to pronounced carcinogenic activity; this property is sometimes very sensitive to modification of molecular structure, whereas in other cases it survives quite gross structural changes. This point may be illustrated by reference to derivatives of 3 : 4-benzpyrene (IV), the active carcinogenic hydrocarbon of coal tar. Its 4′- and 6-methyl derivatives are much slower in action, and its 2′- and 3′-methyl derivatives appear to be without carcinogenic activity.[34] On the other hand, high activity is still retained in 1 : 2 : 3 : 4- and 3 : 4 : 8 : 9-dibenzpyrene.[35]

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[24] O. Kruber, *Angew. Chem.*, 1940, **53**, 69; *Ber.*, 1940, **73**, 1184; 1941, **74**, 1688.

[25] *Ber.*, 1942, **75**, 820; cf. T. Cosciug, *Ann. sci. Univ. Jassy*, Sect. I, 1940, **26**, 415.

[26] I.G., *Brit. Pat.* 453,254; 470,338; 493,307; 493,447; 493,508; 497,089; 510,736; compare K. Zerbe and K. G. Grosskopf, *Brenstoff.-Chem.*, 1938, **19**, 61; E. Berl, H. Biebesheimer, and W. Koerber, *Ind. Eng. Chem.*, 1941, **33**, 672.

[27] Compare E. A. Coulson, *Chem. and Ind.*, 1941, **60**, 699, and O. Kruber, *Ber.*, 1931, **64**, 84.

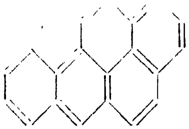
[28] See, *e.g.*, I.G., *Brit. Pat.* 470,338; 497,089.

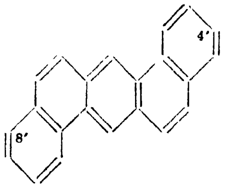
[29] *J. Amer. Chem. Soc.*, 1942, **64**, 1485.

[30] M. S. Newman, *ibid.*, 1940, **62**, 1683.

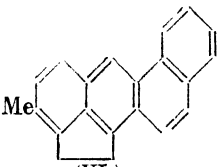
[31] *Ibid.*, 1936, **58**, 1051.

[32] *Ibid.*, 1940, **62**, 2243.


(IV.)

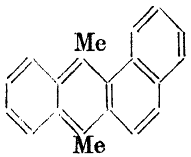


(V.)

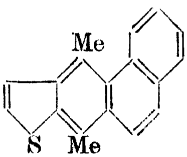


(VI.)

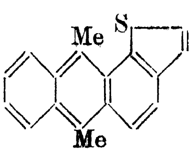
1 : 2 : 5 : 6-Dibenzanthracene (V) is noteworthy as the first polycyclic hydrocarbon found to have carcinogenic activity, and 20-methylcholanthrene * (VI) is of interest as a highly carcinogenic hydrocarbon, related to the sterols and bile acids; it may, in fact, be prepared from cholic and deoxycholic acid, and from cholesterol. 9 : 10-Dimethyl-1 : 2-benzanthracene (VII) is outstanding as the most rapidly acting cancer-producing hydrocarbon so far found, and it is remarkable that a similar high order of activity is shown by the structurally analogous 4 : 9-dimethyl-5 : 6-benzthiophanthren (VIII).[36]



(VII.)



(VIII.)



(IX.)

An analogous compound, 9 : 10-dimethyl-1 : 2-(2′ : 3′-thiopheno)anthracene

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[33] J. W. Cook, E. L. Kennaway, *et al.*, *Amer. J. Cancer*, 1937, **29**, 219; 1938, **33**, 50; 1940, **39**, 381,521; L. F. Fieser, *ibid.*, 1938, **34**, 37.

[34] L. F. Fieser and H. Heymann, *J. Amer. Chem. Soc.*, 1941, **63**, 2333.

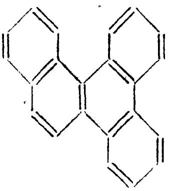
[35] W. E. Bachmann *et al.*, *Proc. Roy. Soc.*, 1937, *B*, **123**, 343.

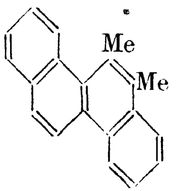
[36] R. B. Sandin and L. F. Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 3098; C. E. Dunlap and S. Warren, *Cancer Research*, 1941, **1**, 953.

* The name *cholanthrene* is derived from the *cholane* (bile acid) group of natural products, and the sterol system of numbering is used for cholanthrene derivatives.

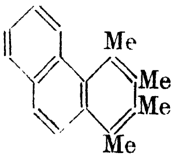
(IX), has been prepared by E. B. Hershberg and L. F. Fieser [37] by a method which could be adapted to the formation of the corresponding compound containing radioactive sulphur. This compound with labelled sulphur would be of value in biochemical investigations.

In the 1 : 2-benzanthracene series it has often been found that a condensed benzene ring is equivalent to two *o*-methyl groups in its influence in promoting carcinogenic activity. The extension of this principle to the 3 : 4-benzphenanthrene series by C. L. Hewett has led to the discovery of simple homologues of chrysene and phenanthrene possessing weak carcinogenic activity. These are 1 : 2-dimethylchrysene (XI) [38] and 1 : 2 : 3 : 4-tetramethylphenanthrene (XII),[39] which are related in the manner indicated to the moderately potently carcinogenic 1 : 2 : 3 : 4-dibenzphenanthrene (X).[40] Moreover, it may be observed that substitution of a condensed benzene ring for the methyl groups at positions 2 and 3 in 1 : 2 : 3 : 4-tetramethylphenanthrene leads to the structure of the very active carcinogenic hydrocarbon 9 : 10-dimethyl-1 : 2-benzanthracene (VII).


(X.)



(XI.)



(XII.)

When carcinogenic hydrocarbons are introduced into the animal body, they become hydroxylated and excreted. The compound obtained thus from 3 : 4-benzpyrene appears to be a monohydroxy-derivative, which has not yet been identified.[41] E. Boyland and his collaborators [42] isolated a dihydroxy-derivative of 1 : 2 : 5 : 6-dibenzanthracene from the urine of rabbits receiving a diet which contained the hydrocarbon. In the case of mice and rats an isomeric dihydroxy-derivative was obtained;[43] this was identical with 4′ : 8′-dihydroxy-1 : 2 : 5 : 6-dibenzanthracene (compare V) synthesised by J. Cason and L. F. Fieser.[44] An interesting feature of these biochemical oxidations is that oxidation takes place at positions which are not those normally attacked by chemical oxidising agents. This is also the case with anthracene, which was found by E. Boyland and A. A. Levi [45] to give various oxidised products in which the *meso*-ring had not been attacked. Possibly the reactive positions normally attacked in chemical oxidation are protected by some kind of conjugation with the enzymes on which the hydrocarbons are adsorbed during biochemical oxidation. In connection with this it may be pointed out that positions 4′ and 8′ of the 1 : 2 : 5 : 6-dibenzanthracene molecule are the positions of substitution when the 9 : 10-quinone is sulphonated.[44]

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[37] *J. Amer. Chem. Soc.*, 1941, **63**, 2561.

[38] C. L. Hewett, *J.*, 1940, 293.

[39] C. L. Hewett and R. H. Martin, *ibid.*, p. 1396.

[40] C. L. Hewett, *J.*, 1938, 193.

[41] J. G. Chalmers and D. Crowfoot, *Biochem. J.*, 1941, **35**, 1270.

[42] E. Boyland, A. A. Levi, E. H. Mawson, and E. Roe, *ibid.*, p. 184.

[43] K. Dobriner, G. I. Lavin, and C. P. Rhoads, *Cancer Research*, 1942, **2**, 79.

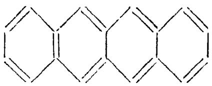
[44] *J. Amer. Chem. Soc.*, 1940, **62**, 2681.

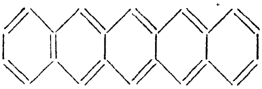
[45] *Biochem. J.*, 1935, **29**, 2679; 1936, **30**, 728.

Structure.

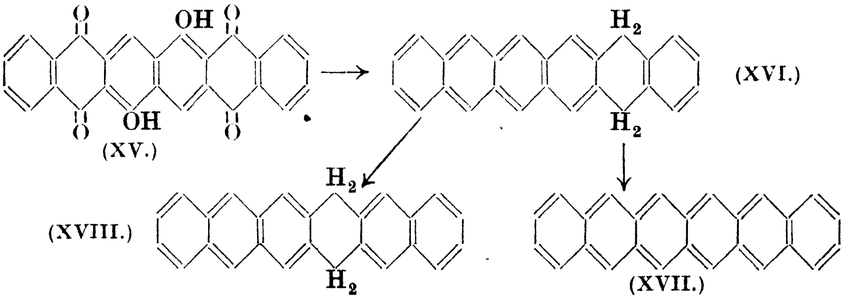
Study of a series of derivatives of naphthacene (2 : 3-benzanthracene) (XIII) by L. F. Fieser [46] showed clearly that attachment of the fourth benzene ring increased the stability of the *meso*-dihydro-structure of anthracene and decreased that of the completely aromatic structure. These differences are enhanced in pentacene (2 : 3 : 6 : 7-dibenzanthracene) (XIV), a deep blue, highly reactive hydrocarbon to which E. Clar and Fr. John [47] assigned the structure of a diradical. That the diradical structure is inadmissible was shown by measurements of magnetic susceptibility carried out by E. Müller and I. Müller-Rodloff,[48] who concluded that the solid hydrocarbon cannot contain more than 1% of a diradical. The series of *linear* benzologues of anthracene has been extended by the synthesis of hexacene (XVII), a deep green hydrocarbon, by E. Clar.[49] Fusion of a mixture of phthalic anhydride and 1 : 5-dihydroxynaphthalene with aluminium chloride–sodium chloride at 200° gives the dihydroxy-diquinone (XV),[50] which on reduction by Clar's elegant method of fusion with zinc chloride, sodium chloride and zinc dust [51] passes into the orange-red dihydrohexacene (XVI), a typical naphthacene derivative. This is dehydrogenated to hexacene (XVII) by sublimation with copper powder. Green solutions of hexacene are sensitive to light and air, and are immediately decolorised by maleic anhydride (cf. p. 190). The orange-yellow solution of dihydrohexacene (XVI) becomes appreciably paler when boiled, and this is attributed to isomerisation to (XVIII).

(XIII.)





(XIV.)



C. Marschalk [49] obtained the orange dihydrohexacene (XVI) by reduction of a tetrahydroxyhexacenequinone which he prepared by condensation of

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[46] *J. Amer. Chem. Soc.*, 1931, **53**, 2329.

[47] *Ber.*, 1930, **63**, 2967.

[48] *Annalen*, 1935, **517**, 134.

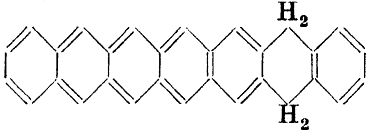
[49] *Ber.*, 1939, **72**, 1817; see also *ibid.*, 1942, **75**, 1283; cf. C. Marschalk, *Bull. Soc. chim.*, 1939, **6**, 1112.

[50] E. Clar, U.S.P. 2,210,396.

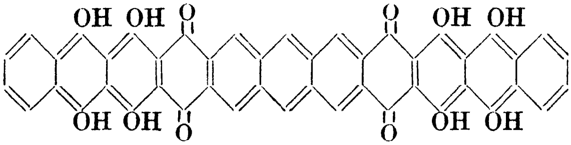
[51] *Ber.*, 1939, **72**, 1645.

leuco-quinizarin with naphthalene-2 : 3-dicarboxylic anhydride or of *leuco*-naphthaquinizarin with phthalic anhydride. By similar condensation of *leuco*-quinizarin with anthracene-2 : 3-dicarboxylic anhydride he obtained [52] a tetrahydroxyheptacenequinone, and with *leuco*-naphthaquinizarin the product was a tetrahydroxyoctacenequinone. The parent hydrocarbons, heptacene * and octacene, have not been described, although Marschalk prepared colourless hexa- and tetra-hydrides of heptacene, as well as its blue-violet dihydride (probably XIX).

(XIX.)



By condensation of the dianhydride of anthracene-2 : 3 : 6 : 7-tetracarboxylic acid with *leuco*-quinizarin, Marschalk [53] obtained a diquinone (XX) in which there are no fewer than 11 *linear* condensed rings.



(XX.)

In their deep colour and high reactivity these linear benzologues of anthracene are in striking contrast to the colourless and comparatively inert *angular* benzologues (*e.g.*, 1 : 2-benz- and 1 : 2 : 5 : 6-dibenz-anthracene). The reaction of naphthacene, pentacene and hexacene, but not of anthracene, with sulphur to give products which no longer have the characteristics of the parent hydrocarbons is a further illustration of the reactivity of these *linear* benzologues of anthracene.[54] Thus, pentacene reacts with sulphur in boiling trichlorobenzene to give a microcrystalline green pigment containing approximately six atoms of sulphur combined in a molecule of pentacene.

These differences in reactivity of the benzologues of anthracene are doubtless related to their bond structure, which E. Clar [55] has attempted to correlate with their absorption spectra. He points out [56] that the quinone corresponding to a very reactive hydrocarbon has very little reactivity, and vice versa. Naphthacenequinone (XXXIII) is converted into a vat (*i.e.*, an alkaline solution of the quinol) only with difficulty; pentacenequinone does not give a vat. The reactivity of a quinone, *i.e.*, its tendency to attract hydrogen, is determined by its reduction potential. Clar has developed numerical relationships from which he claims that it is possible to predict the absorption spectrum (*i.e.*, the colour) and reactivity of one of these hydrocarbons, and also the reduction potential of the quinone, even when the

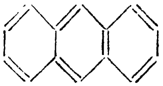
[52] *Bull. Soc. chim.*, 1941, **8**, 354. [53] *Ibid.*, 1942, **9**, 400. [54] *Idem, ibid.*, 1939, **6**, 1122.

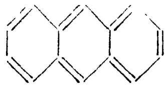
[55] *Ber.*, 1936, **69**, 607; 1940, **73**, 81, 596. [56] *Ber.*, 1940, **73**, 104.

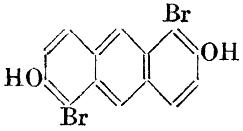
* The synthesis of heptacene, an "ultra-green" hydrocarbon, has been described in a paper which became available after this Report was written (E. Clar, *Ber.*, 1942, **75**, 1330). The compound has the expected high reactivity, and in a vacuum at 320° it disproportionates to give a dihydride of heptacene.

hydrocarbon and its quinone are both unknown. For details of these relationships the original papers should be consulted. It will be noted that when more than two rings are fused in a *linear* condensation it becomes impossible to represent them all by Kekulé formulæ, and a "polyene" type of system develops. This condition does not result from *angular* fusion of rings.

The bond-structures of polycyclic aromatic hydrocarbons and their quinones have been investigated by both chemical and physical methods. The chemical reactivity of anthracene is higher than that of phenanthrene, and this is reflected in their respective heats of combustion; the value for anthracene is some 7 kg.-cals. greater than that for phenanthrene.[57] Clearly this is related to the fact that in the *angular* structure, but not the *linear* structure, it is possible for all three rings to be completely benzenoid in character. In terms of Kekulé formulæ the bond-structures (XXI) and (XXII) for anthracene are open for consideration. Of these, K. Fries, R. Walter, and K. Schilling [57] preferred the first (XXI), as there is a closer average approach to the stable condition of an isolated benzene ring. To test this, they studied the bromination of 2 : 6-dihydroxyanthracene and obtained the 1 : 5-dibromo-compound (XXIII). This was regarded as supporting formula (XXI); the disposition of double bonds in the alternative formula would favour 3 : 5-substitution. As is justly pointed out by L. F. Fieser and W. C. Lothrop,[58] this evidence is inconclusive, as the two bond-structures may be tautomeric with one of them predominating or more readily substituted. In an attempt to resolve this uncertainty the American workers applied a type of method which they had previously used to study the bond-structure of naphthalene.[59] They found that neither the 1 : 5-dimethyl nor the 1 : 5-diallyl derivative of 2 : 6-dihydroxyanthracene would couple with diazotised sulphanilic acid or *p*-nitroaniline and concluded that tautomerism is negligible and that these anthracene derivatives have the bond-structure shown in formula (XXIII). If the tetrasubstituted anthracenes were derived from the structure (XXII), then diazo-coupling at a free β-position would be expected. It is assumed that the parent hydrocarbon likewise has the bond-structure (XXI). This conception of fixed double bonds will hardly find general acceptance, but the growing body of evidence that condensed-ring polycyclic compounds do, in fact, behave as if their molecules contained fixed double bonds cannot be discounted. In the case of anthracene the position is perhaps expressed by the statement that the bond-structure (XXI) is the one which makes the predominant contribution to the resonance state of the molecule.


(XXI.)


(XXII.)



(XXIII.)

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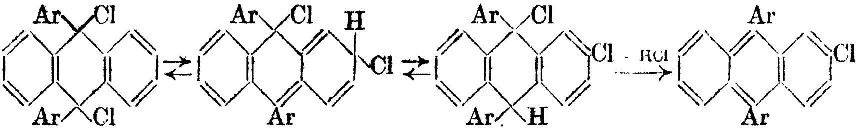
[57] *Annalen*, 1935, **516**, 248.

[58] *J. Amer. Chem. Soc.*, 1936, **58**, 749.

[59] L. F. Fieser and W. C. Lothrop, *ibid.*, 1935, **57**, 1459.

An interesting type of tautomerism in the anthracene series has been described by E. Bergmann and (Mrs.) O. Blum-Bergmann,[60] who found that the *meso*-dichlorides (XXIV) of 9 : 10-diphenyl- and 9 : 10-di-α-naphthyl-anthracene lose hydrogen chloride to give the 2-chloro-9 : 10-diarylanthracene (XXV). This is interpreted as follows:

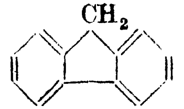


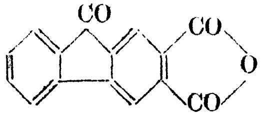
(XXIV.) (XXV.)

It is concluded from dipole measurements that the dichloride of 9 : 10-diphenylanthracene (XXIV) has the *cis*-configuration (cf. p. 174).

The bond-structure of fluorene (XXVI) was studied by W. C. Lothrop,[61] who considered that this problem should be susceptible to the methods of investigation used by Fieser and Lothrop [62] for other polycyclic structures; namely, rearrangement of allyl ethers, and diazo-coupling of hydroxy-derivatives. It was concluded that there is little or no fixation of double bonds, in which respect fluorene resembles benzene, tetralin and indane, rather than naphthalene, anthracene and phenanthrene. W. C. Lothrop and J. A. Coffman [63] failed to find any evidence that the Mills–Nixon effect was operating to cause strain in the anhydride ring of fluorenone-2 : 3-dicarboxylic anhydride (XXVII).

(XXVI.)

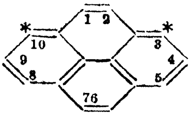


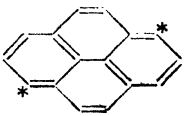


(XXVII.)

A comprehensive investigation of the chemistry of pyrene was made by H. Vollmann, H. Becker, M. Corell, and H. Streeck.[64] The bond-structures (XXVIII) and (XXIX) are consistent with the chemical reactivity of pyrene, including its degradation by ozone.[65] The failure of 3-hydroxy-pyrene to undergo diazo-coupling suggests bond-fixation, in which case the hydroxyl group would occupy one of the asterisked positions.

(XXVIII.)





(XXIX.)

Incidentally these are the positions which are attacked when two substituents are introduced into the pyrene molecule; mixtures of 3 : 8- and 3 : 10-compounds are invariably formed.

The mode of interaction of carbonyl compounds with organometallic compounds has also been used to determine the effective bond-structures of polycyclic aromatic compounds. The observation of G. Charrier and E. Ghigi[66] that addition of methylmagnesium iodide to the carbonyl group of *meso*-benzanthrone is accompanied by 1 : 4-addition has been extended by C. F. H. Allen and S. C. Overbaugh,[67] who showed that both phenylmagnesium bromide and benzylmagnesium chloride, as well as *n*-heptylmagnesium bromide and *cyclo*hexylmagnesium chloride, react with *meso*-benzanthrone (XXXI) to give 4-substituted derivatives (XXX). Similar results were obtained[68] in the interaction of Grignard reagents with 1′-phenyl*meso*benzanthrone. In many cases high yields of the 4-derivatives are obtained and Allen and Overbaugh consider that this indicates that *meso*-benzanthrone must have the bond-structure shown in formula (XXX) or (XXXI).

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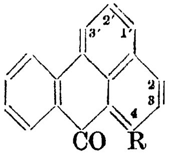
[60] *J. Amer. Chem. Soc.*, 1937, **59**, 1439. [61] *Ibid.*, 1939, **61**, 2115.

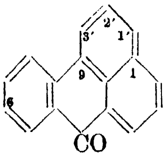
[62] *Ibid.*, 1936, **58**, 749, 2050; 1937, **59**, 945.

[63] *Ibid.*, 1941, **63**, 2564. [64] *Annalen*, 1937, **531**, 1.

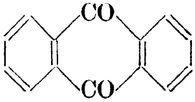
[65] See also L. F. Fieser and F. C. Novello, *J. Amer. Chem. Soc.*, 1940, **62**, 1855.



(XXX.)



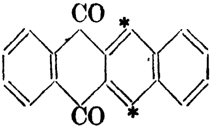
(XXXI.)



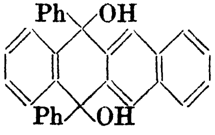
(XXXII.)

The first of these accords with the usual bond-structure of naphthalene, and is also compatible with the failure of *meso*-benzanthrone to combine with maleic anhydride.

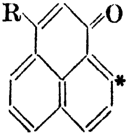
Anthraquinone reacts with Grignard reagents exclusively by addition to the carbonyl group, which indicates the bond-structure (XXXII). In the case of naphthacenequinone the presence of a naphthalene system disturbs the normal anthraquinone bond structure, and in agreement with the formulation (XXXIII), C. F. H. Allen and L. Gilman[69] found that naphthacenequinone adds on phenylmagnesium bromide (phenyl groups at the positions asterisked) to give a tetrahydroquinone which is oxidised by air in alkaline suspension to a diphenylnaphthacenequinone. Further study of this Grignard condensation[70] showed that the normal diol (XXXIV) is also formed but in the presence of magnesium this diol is reduced (apparently by the Gomberg reagent, Mg + $MgBr_2$)[71] to diphenylnaphthacene. This reduction of diols is peculiar to the products from naphthacenequinone and a tetrahydronaphthacenequinone, and is associated with the abnormal bond-structure.



(XXXIII.)



(XXXIV.)



(XXXV.)

(R = H, OMe or OEt.)

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[66] *Gazzetta*, 1932, **62**, 928.

[67] *J. Amer. Chem. Soc.*, 1935, **57**, 740.

[68] *Idem, ibid.*, p. 1322.

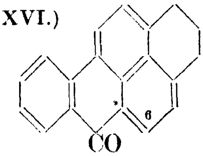
[69] *Ibid.*, 1936, **58**, 937.

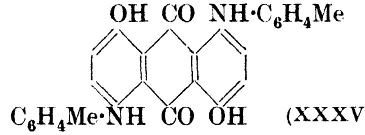
[70] C. F. H. Allen and A. Bell, *ibid.*, 1940, **62**, 2408.

[71] Compare M. Gomberg and W. E. Bachmann, *ibid.*, 1927, **49**, 236.

1 : 4-Addition of Grignard reagents is also shown by 2 : 3 : 6 : 7-dibenzanthraquinone (pentacenequinone) and its derivatives,[72] although phenyl-lithium reacts normally, and by perinaphthenone * derivatives of the type (XXXV), which react with phenylmagnesium bromide with introduction of a phenyl group at the asterisked position.[73] In the case of a 3 : 4-benzpyrene derivative related to *meso*-benzanthrone (XXXVI) even methyl-lithium leads to 1 : 4-addition as well as addition to the carbonyl group, so that a methyl group may be introduced into position 6.[74]

(XXXVI.)





(XXXVII.)

The structure of some anthraquinone acid dyes has been the subject of an interesting series of papers by C. F. H. Allen and his collaborators.[75] These were concerned primarily with toluidine-blue and toluidine-green, little-used dyes which had long been on the market but their constitution had not been disclosed. Toluidine-blue has certain absorption spectral characteristics which distinguish it from other blue dyes. Elementary analysis of the purified blue dye gave the formula $C_{28}H_{20}O_{10}N_2S_2Na_2$; it forms a yellow vat; the zinc dust fusion reduction method of Clar [51] gave anthracene, a sulphide, and a purple solid, $C_{28}H_{22}O_4N_2$. This indicated that the dye is a sulphonated anthraquinone derivative. " Oxidative hydrolysis " with concentrated nitric acid gave 1 : 4 : 5 : 8-tetrahydroxyanthraquinone, the structure of which was proved by its synthesis from 3 : 6-dimethoxyphthalic anhydride and quinol. The purple product, $C_{28}H_{22}O_4N_2$, was shown by its synthesis from 4 : 8-dichloroanthrarufin and *p*-toluidine to be 1 : 5-di-*p*-toluidino-4 : 8-dihydroxyanthraquinone (XXXVII), and from it toluidine-blue was obtained by sulphonation. Toluidine-green was similarly shown to be the corresponding 1 : 4-di-*p*-toluidino-5 : 8-dihydroxy-compound. Finally, " reductive hydrolysis " of toluidine-blue by tin and hydrochloric acid gave *leuco*-1 : 4 : 5 : 8-tetrahydroxyanthraquinone and 4-aminotoluene-3-sulphonic acid, by which the positions of the two sulphonic acid groups were established.

Comparison of the absorption spectra of these two dyes with others of somewhat similar structure enabled further conclusions to be drawn. α-Hydroxyl groups have a much greater influence on the absorption spectrum than β-hydroxyl groups, an effect which is attributed to chelation with the adjacent carbonyl group. In the case of the sulphonated dyes a sodium sulphonate group at position 2′ has a markedly different effect from that of the same group at position 3′ or 4′. This is regarded as indicating a hydrogen bond involving the imino-hydrogen, so that the complete structure (XXXVIII) is assigned to the anion of toluidine-blue. An analogous structure may be given to toluidine-green. It is suggested that in the isomeric 3′- and 4′-sulphonates the imino-hydrogen may be bonded to the carbonyl oxygen, as in (XXXIX) or (XL).

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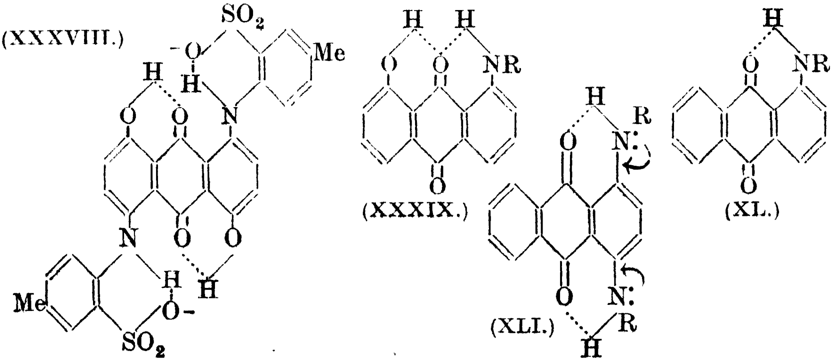
[72] C. F. H. Allen and A. Bell, *J. Amer. Chem. Soc.*, 1942, **64**, 1253.

[73] C. F. Koelsch and R. H. Rosenwald, *ibid.*, 1937, **59**, 2166; *J. Org. Chem.*, 1938, **3**, 462; C. F. Koelsch and J. A. Anthes, *ibid.*, 1941, **6**, 558.

[74] L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, 1938, **60**, 2542.

[75] C. F. H. Allen, G. F. Frame, and C. V. Wilson, *J. Org. Chem.*, 1941, **6**, 732; 1942, **7**, 63; C. F. H. Allen, C. V. Wilson, and G. F. Frame, *ibid.*, 1942, **7**, 68, 169.

* The nomenclature of this ring system was discussed by J. W. Cook and C. L. Hewett (J., 1934, 368). In the present report the system proposed by L. F. Fieser and E. B. Hershberg (*J. Amer. Chem. Soc.*, 1938, **60**, 1659) is used, whereby 1 : 8-trimethylenenaphthalene is termed " perinaphthane."



(XXXVIII.) (XXXIX.) (XLI.) (XL.)

1 : 5-Di-*p*-toluidinoanthraquinone has a smooth absorption curve for the main band in the visible region of the spectrum, whereas the 1 : 4-compound shows two maxima on this band. This double head appears only when both positions 1 and 4 have substituents which are able to furnish electrons by a mesomeric shift (XLI). Sulphonation at positions 3′ and 4′ restrains this mesomeric shift on account of the strong inductive effect of the positive sulphur atom, transmitted to nitrogen through the aromatic ring. If the sulphonic acid group is at position 2′, hydrogen bond formation (XXXVIII) will result in a tendency for the hydrogen to release its electrons shared with nitrogen, thus neutralising the inductive effect of the sulphonic acid group. Allen and his collaborators give a considerable body of spectroscopic data which are in accord with these theoretical views.

The structures of some metallic "lakes" of alizarin have been studied by W. F. Beech and H. D. K. Drew.[76]

Mesomerism is invoked by R. Scholl to account for the marked differences in colour between two series of salts of hydroxyanthraquinones with ammonia and amines [77] and a re-interpretation of the structures of the variously coloured anthraquinol-α-carboxylic acid lactones and their salts is also given.[78] Space does not permit of a summary of this work.

The unsymmetrical structure (XLII) for picenequinone was established by J. W. Cook [79] who showed that its degradation product, picylene ketone,

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[76] *J.*, 1940, 603.

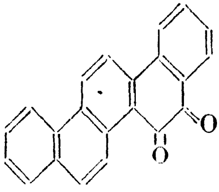
[77] R. Scholl and P. J. Dahll, *Ber.*, 1941, **74**, 1129; R. Scholl, *ibid.*, p. 1171.

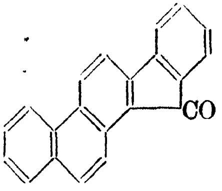
[78] R. Scholl, K. Meyer, and C. Seer, *ibid.*, p. 1182.

[79] *J.*, 1941, 685.

is identical with a synthetic specimen of 2′ : 1′-naphtha-1 : 2-fluorenone (XLIII).[80]

(XLII.)





(XLIII.)

Molecular Compounds.

The problem of the structures of the highly coloured molecular compounds of polycyclic aromatic hydrocarbons with polynitro-compounds has long attracted attention.[81] J. Weiss [82] has recently suggested that these molecular compounds are ionic in character, the coloured positive ion being formed by transfer of an electron from the hydrocarbon (donor) molecule to the molecule of the polynitro-compound. This simple theory has much to commend it, but lacks experimental verification. In an earlier publication [83] Weiss described a dark brown perchlorate of anthracene which he formulated as $[C_{14}H_{10}]^+[ClO_4]^-$, the formation of the positive ion being attributed here to loss of an electron by oxidation. There is no evidence that oxidation is concerned in the formation of this complex, and in the opinion of the Reporter the compound probably contains perchloric acid, rather than the perchlorate ion.

Highly coloured addition compounds of polycyclic compounds with bromine and iodine have been described. The halogen in these is loosely bound and may be removed by treatment with sodium thiosulphate. These complexes are probably of the same type as those formed with polynitro-compounds. Substances which have been found to give these unstable coloured halogenides include *meso*-benzanthrone (XXXI),[84] perinaphthenone (XXXV; R = H),[85] perylene * (XLV),[86] anthanthrene (XLIV) [87] and 10 : 10′-dihydro-9 : 9′-diphenanthrylidene (XLVI).[88] **Highly coloured molecular compounds of polycyclic hydrocarbons [1 : 2- and 2 : 3-benzanthracene, 9 : 9′-dianthranyl, 1 : 12-benzperylene (I), 2 : 3 : 10 : 11-dibenzperylene] with antimony pentachloride and (in some cases) stannic chloride have been** described by K. Brass and K. Fanta.[89] Possibly these have structures of the same type as those of the complexes of polynitro-compounds. The Reporter has observed that pyrene and 1 : 2-benzanthracene readily form crystalline complexes with antimony trichloride; the complex from pyrene is colourless. H. Beyer and J. Richter [90] have described a hexacyclic hydrocarbon which gives a colour with antimony trichloride. Perinaphthenone (XXXV; R = H), in contrast to *meso*-benzanthrone (XXXI), has marked basic properties [91] and forms a series of coloured salts with mineral acids.[92]

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[80] J. W. Cook, C. L. Hewett, W. V. Mayneord and E. Roe, *J.*, 1934, 1727.

[81] See *Ann. Reports*, 1931, **28**, 134.

[82] *J.*, 1942, 245.

[83] *Nature*, 1941, **147**, 512.

[84] K. Brass and E. Clar, *Ber.*, 1936, **69**, 690.

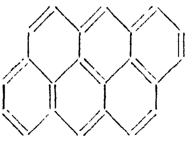
[85] *Idem*, *Ber.*, 1939, **72**, 1882; A. M. Lukin, *Compt. rend. Acad. Sci.*, *U.R.S.S.*, 1940, **28**, 60.

[86] K. Brass and E. Clar, *Ber.*, 1932, **65**, 1660; A. Zinke, H. Troger, and E. Posch, *Ber.*, 1941, **74**, 107; M. Pestemer and E. Treiber, *ibid.*, p. 964.

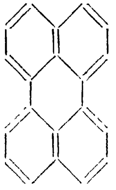
[87] K. Brass and E. Clar, *Ber.*, 1939, **72**, 1882.

[88] E. Bergmann and F. Bergmann, *J. Amer. Chem. Soc.*, 1937, **59**, 1440.

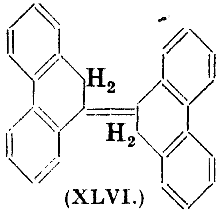
* In the case of perylene (XLV) complications are caused by addition of bromine to "unsaturated" centres, followed by elimination of hydrogen bromide, so that substitution of bromine for hydrogen accompanies molecular compound formation.



(XLIV.)



(XLV.)



(XLVI.)

In connection with the structure of these coloured molecular compounds the choleic acids which some of the polycyclic hydrocarbons form when crystallised with deoxycholic acid are of interest.[93] It by no means follows that these curious compounds, which contain from 2 to 4 molecules of deoxycholic acid combined with 1 molecule of hydrocarbon, possess the same type of structure as the complexes of hydrocarbons with polynitro-compounds. It is significant that, unlike picrates, which are completely dissociated by alkali, the choleic acids are sufficiently stable to form water-soluble sodium salts.[94] W. Marx and H. Sobotka [95] adduce evidence that choleic acids are completely dissociated in solution.

Stereochemistry and Steric Factors.

The characteristic ultra-violet absorption spectrum of diphenyl is associated with a planar molecule, for M. Pestemer and E. Mayer-Pitsch [96] and M. T. O'Shaughnessy and W. H. Rodebush [97] found that in *o*-substituted diphenyl derivatives in which rotation is restricted so that the rings are not co-planar, the diphenyl spectrum is no longer exhibited and the two halves of the molecule behave as independent resonators. These observations have been used by R. N. Jones [98] in a spectroscopic study of the configuration of some condensed ring systems. The spectrum of 9 : 10-dihydrophenanthrene (XLVII) is very similar to that of diphenyl, from which the inference is drawn that the two aromatic rings approximate to a co-planar configuration.

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[89] *Ber.*, 1936, **69**, 1.

[90] *Ber.*, 1940, **73**, 1319.

[91] J. W. Cook and C. L. Hewett, *J.*, 1934, 369.

[92] A. M. Lukin, *Bull. Acad. Sci. U.R.S.S., Classe sci. chim.*, 1941, 411.

[93] L. F. Fieser and M. S. Newman, *J. Amer. Chem. Soc.*, 1935, **57**, 1602.

[94] See also A. Winterstein and H. Vetter, *Z. physiol. Chem.*, 1934, **230**, 169; L. F. Fieser and A. M. Seligman, *J. Amer. Chem. Soc.*, 1936, **58**, 2486.

[95] *J. Org. Chem.*, 1936, **1**, 275.

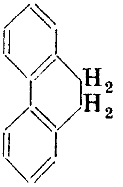
[96] *Monatsh.*, 1937, **70**, 104.

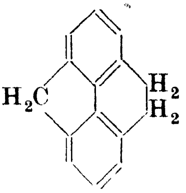
[97] *J. Amer. Chem. Soc.*, 1940, **62**, 2906.

[98] *Ibid.*, 1941, **63**, 1658.

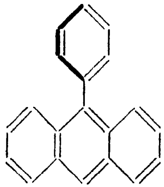
This is likewise the case with 4 : 5-methylene-9 : 10-dihydrophenanthrene (XLVIII); hence any distortion from the planar configuration which the strain in the 5-membered ring might tend to produce is effectively prevented by an opposing influence of the second bridge. Jones found that the absorption spectrum of anthracene is practically unaltered by aryl substitution in the *meso*-positions (9-phenyl- and 9 : 10-diphenyl-anthracene; 9 : 9′-dianthranyl). He therefore concludes that the planes of the *meso*-aryl groups are inclined to that of the anthracene system, as indicated in (XLIX) for 9-phenylanthracene. The same considerations hold for rubrene (L), the spectrum of which closely resembles that of the unsubstituted hydrocarbon, naphthacene.[99] A non-planar configuration of rubrene is supported by *X*-ray crystallographic evidence.[1]

(XLVII.)

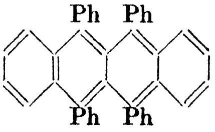




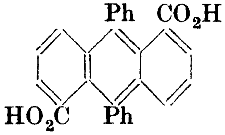
(XLVIII.)



(XLIX.)



(L.)



(LI.)

A steric influence of *meso*-aryl groups on substituents in the lateral rings of the anthracene system is shown in the case of 9 : 10-diphenylanthracene-1 : 5-dicarboxylic acid (LI), which cannot be esterified by alcohol and acid.[2] The ester, obtained through the silver salt, is extremely resistant to hydrolysis, 90% being recovered unchanged after 30 hours' boiling with 25% methyl-alcoholic potash.

A striking example of the influence of spatial factors on chemical reactivity is found in the Diels–Alder addition product (LII) of 9-bromoanthracene and maleic anhydride. This adduct was prepared by E. de B. Barnett, N. F. Goodway, A. G. Higgins, and C. A. Lawrence *[3] and found by them to give no ionised halogen after 40 minutes' boiling with alcoholic potash. The adduct of 9 : 10-dichloroanthracene showed similar resistance, although E. Clar[4] had found that the chlorine atoms are displaced by aryl

[99] C. Dufraisse and R. Horclois, *Bull. Soc. chim.*, 1936, **3**, 1880.

[1] E. Bergmann and E. Herlinger, *J. Chem. Physics*, 1936, **4**, 532.

[2] R. Scholl, H. K. Meyer, and W. Winkler, *Annalen*, 1932, **494**, 201.

[3] *J.*, 1934, 1224.

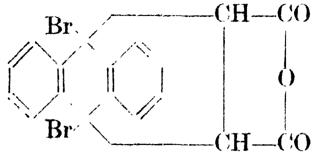
[4] *Ber.*, 1931, **64**, 2194.

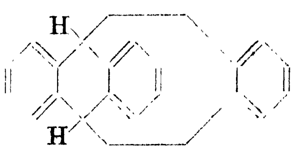
* These authors prepared the adduct in boiling *o*-dichlorobenzene, but do not mention the yield. W. E. Bachmann and M. C. Kloetzel (*J. Org. Chem.*, 1938, **3**, 55) obtained an almost theoretical yield in boiling xylene.

groups in the Friedel–Crafts reaction. P. D. Bartlett and S. G. Cohen[5] reinvestigated the behaviour of (LII) and found that treatment for 15–18 hours with boiling 15—30% potassium hydroxide solution had no other effect than to open the anhydride ring and isomerise the *cis*-dibasic acid into the *trans*-acid.[6] In fact, the bromine atom in this compound was found to be at least a million times less reactive than the bromine atom in 9-bromo-9-methylfluorene. This is in marked contrast to the well-known lability normally shown by bromine atoms in the *meso*-positions of 9 : 10-dihydroanthracene.

Chemical inertness is shown also by the adducts of 9-nitro- and 9-acetamido-anthracene with maleic anhydride; for example, the nitro-compound is not reduced by stannous chloride. Bartlett and Cohen point out that these adducts are among the few compounds which are structurally incapable of replacement reactions accompanied by Walden inversion. This circumstance may account for the inertness of the bromine in (LII), but can hardly explain the resistance to reduction shown by the corresponding nitro-compound. F. Bergmann[7] found that the adduct of anthracene with maleic anhydride does not undergo the dehydrogenation with nitrobenzene characteristic of many other hydroaromatic structures formed in diene syntheses.[8]

(LII.)





(LIII.)

An interesting hydrocarbon with a multiplanar molecule (LIII) has been described recently by P. D. Bartlett, M. J. Ryan, and S. G. Cohen.[9] This was obtained by reduction, through a series of intermediates, of the Diels–Alder adduct of anthracene and *p*-benzoquinone. It was given the name triptycene (from *triptych*), and it was found that the *meso*-hydrogen atoms show none of the reactivity of the similarly linked hydrogen of triphenylmethane. There was no exchange with phenyl*iso*propylpotassium, and no chlorination by sulphuryl chloride in presence of benzoyl peroxide. Oxidation with chromic acid gave only anthraquinone and carbon dioxide. Intermediate hydroxy-compounds analogous to triphenylcarbinol were not formed. The anomalous behaviour is attributed to a damping of resonance by the structural rigidity, with a preference for the bond structure shown in (LIII).

The question of the configuration of the fluorene molecule was revived by

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[5] *J. Amer. Chem. Soc.*, 1940, **62**, 1183.

[6] Compare O. Diels and K. Alder, *Annalen*, 1931, **486**, 191.

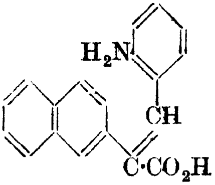
[7] *J. Amer. Chem. Soc.*, 1942, **64**, 176.

[8] Compare E. Clar, *Ber.*, 1936, **69**, 1686; E. Bergmann, L. Haskelberg, and F. Bergmann, *J. Org. Chem.*, 1942, **7**, 303.

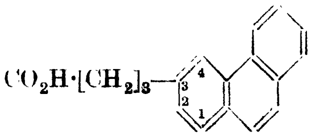
[9] *J. Amer. Chem. Soc.*, 1942, **64**, 2649.

J. Iball's examination[10] of the crystal structure of fluorene by *X*-ray analysis. The data which he obtained accord with a structure in which the aromatic nuclei are inclined to one another at an angle of about 20°, but are difficult to reconcile with a planar molecule. Thus in the solid state fluorene appears to have a non-planar configuration, and the stereochemical implications of this were discussed by J. W. Cook and J. Iball,[11] who reviewed the literature of attempts to prepare stereoisomeric fluorene derivatives dependent on such a non-planar configuration. The dipole moments of fluorene, fluorenone and a number of derivatives were measured by E. D. Hughes, (Mrs.) C. G. Le Fèvre, and R. J. W. Le Fèvre,[12] who were able to exclude a number of possible configurations, but their results (obtained with solutions) neither supported nor excluded a non-planar configuration. A non-planar configuration would tend to relieve the strain in the 5-membered ring, but would imply an unprecedented distortion of the valency directions of benzene out of the plane of the aromatic ring.

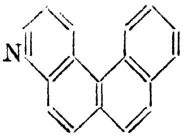
Spatial influences have been encountered in investigations relating to the synthesis and reactions of a number of polycyclic aromatic compounds. Thus in the application of the Pschorr phenanthrene synthesis to the acid (LIV) ring-closure takes place mainly at the β-position of the naphthalene ring and only to a lesser extent at the more reactive α-position. Accordingly, the 1 : 2-benzanthracene structure is formed in addition to the 3 : 4-benzphenanthrene structure.[13] The cyclisation of γ-3-phenanthrylbutyric acid (LV) takes place almost exclusively at position 2, with the formation of a ketotetrahydro-1 : 2-benzanthracene.[14] That failure to cyclise at position 4 is not due to chemical inertness at this position is shown by the fact that position 4 is attacked when 3-aminophenanthrene is submitted to the Skraup reaction, the product being represented by (LVI).[15] Also W. E. Bachmann and M. C. Kloetzel[16] found that cyclisation of the chloride of β-3-phenanthrylpropionic acid occurred at position 4 exclusively.



(LIV.)



(LV.)



(LVI.)

Other examples of the phenomenon just discussed were furnished by γ-8-methyl-2-naphthylbutyric acid (LVII)[17] and γ-5 : 6 : 7 : 8-tetramethyl-2-naphthylbutyric acid (LVIII),[18] which undergo cyclisation at position 3 to give an anthracene derivative, whereas the parent γ-2-naphthylbutyric acid undergoes ring-closure at position 1 to give a phenanthrene derivative.

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[10] *Z. Krist.*, 1936, *A*, **94**, 397.

[11] *Chem. and Ind.*, 1936, **55**, 467.

[12] *J.*, 1937, 202.

[13] J. W. Cook, *J.*, 1931, 2524.

[14] R. D. Haworth and C. R. Mavin, *J.*, 1933, 1012.

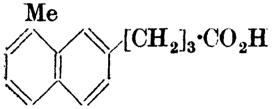
[15] E. Mosettig and J. W. Kreuger, *J. Org. Chem.*, 1938, **3**, 317.

[16] *J. Amer. Chem. Soc.*, 1937, **59**, 2207.

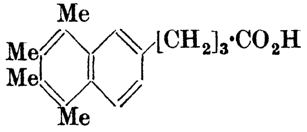
[17] R. D. Haworth and G. Sheldrick, *J.*, 1934, 1950.

[18] C. L. Hewett, *J.*, 1940, 293.

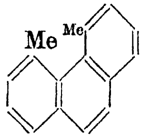
The experiment with (LVII) was made in the course of an unsuccessful attempt to synthesise 4 : 5-dimethylphenanthrene (LIX). Introduction of two methyl groups in these 4 : 5-positions would impose considerable strain on the molecule and could not be effected without distortion. Even the Pschorr reaction failed to give this type of structure, for the amino-acid (LX) did not undergo ring-closure under the usual conditions.[19] The chemical behaviour of the few known 4 : 5-substituted phenanthrenes is governed by these considerations of spatial configuration. Thus, 4-phenanthraldehyde-5-carboxylic acid (LXI), obtained by ozonisation of pyrene,[20] is stable to alkaline oxidation, and is readily transformed back into pyrene derivatives. Treatment with alcoholic potash or potassium cyanide gives 1 : 2-pyrenequinone (LXII), whereas hydrazine hydrate gives 1-hydroxypyrene (LXV).



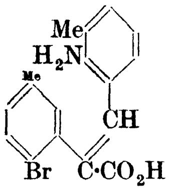
(LVII.)



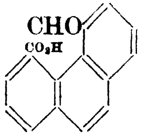
(LVIII.)



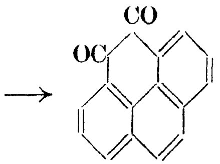
(LIX.)



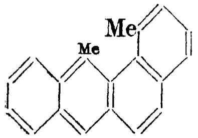
(LX.)



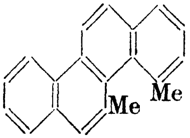
(LXI.)



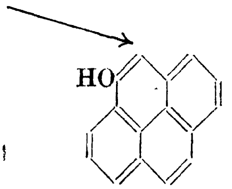
(LXII.)



(LXIII.)



(LXIV.)



(LXV.)

Unsuccessful attempts have been made to synthesise 1′ : 9-dimethyl-1 : 2-benzanthracene (LXIII), of analogous structure to 4 : 5-dimethylphenanthrene.[21] M. S. Newman [22] has succeeded, however, in synthesising a hydrocarbon which is believed to be the similarly constituted 6 : 7-dimethylchrysene (LXIV).* Its ultra-violet absorption spectrum was examined by

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[19] E. E. Lewis and R. C. Elderfield, *J. Org. Chem.*, 1940, **5**, 290.

[20] H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Annalen*, 1937, **531**, 66; compare L. F. Fieser and F. C. Novello, *J. Amer. Chem. Soc.*, 1940, **62**, 1855.

[21] L. F. Fieser and A. M. Seligman, *ibid.*, 1938, **60**, 170; 1939, **61**, 136.

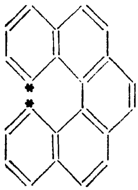
[22] *Ibid.*, 1940, **62**, 2295.

* In the original paper the Patterson system of numbering is used, so that the compound is described as 4 : 5-dimethylchrysene.

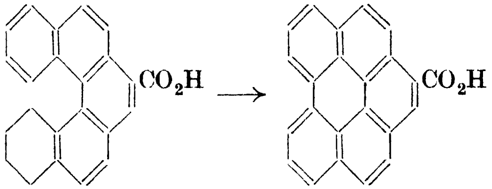
R. N. Jones,[23] who found that it had the chrysene type of spectrum, which, nevertheless, differs in some respects from those of other methylchrysenes. Clearly the molecule of this dimethylchrysene must be distorted, either by modification of the angles of the aromatic rings, or by accommodating the methyl groups in a non-planar configuration. If the latter be the case, then a compound of this type may exist in optically active forms, a possibility to which Newman drew attention. Similarly situated methyl groups in more complex ring systems were already known.[24] Doubtless in the more complex molecules their greater flexibility enables the strain to be distributed throughout the ring system.

Somewhat similar considerations should apply in the case of 3 : 4 : 5 : 6-dibenzphenanthrene (LXVI). In an undistorted molecule there would be no room for the hydrogen atoms at the asterisked positions, for the distance between the two carbon atoms would be the ordinary interatomic distance of the carbon atoms of a benzene ring. Consequently this hydrocarbon should undergo very ready dehydrogenation to 1 : 12-benzperylene (I). Although 3 : 4 : 5 : 6-dibenzphenanthrene is known,[25] this conversion has not been recorded. That such a tendency does exist was shown, however, in the case of a carboxylic acid (LXVII) derived from a tetrahydroxy-3 : 4 : 5 : 6-dibenzphenanthrene; this acid on dehydrogenation with sulphur lost *six* hydrogen atoms to give a 1 : 12-benzperylenecarboxylic acid (LXVIII).[26]

Of interest in this connection is Newman's synthesis [30] (p. 157) of coronene (II) from a 3 : 4 : 5 : 6-dibenzphenanthrene derivative (LXIX) by heating with fused potassium hydroxide. It will be noted that the hypothetical intermediate 1 : 10-benzperylene derivative contains methyl groups in positions equivalent to the 4 : 5-positions of phenanthrene. These methyl groups suffer loss of hydrogen to form the final ring of coronene.

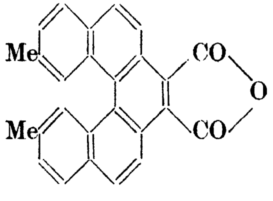


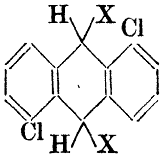
(LXVI.)



(LXVII.) (LXVIII.)

(LXIX.)





(LXX.)

(X = Cl, Br or OH)

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[23] *J. Amer. Chem. Soc.*, 1941, **63**, 313.

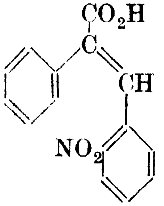
[24] R. Scholl and C. Tänzer, *Annalen*, 1923, **433**, 172; D.R.-P. 458,710; compare R. Scholl and K. Meyer, *Ber.*, 1934, **67**, 1232.

[25] J. W. Cook, *J.*, 1933, 1592.

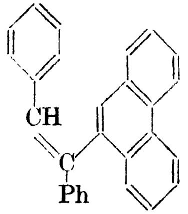
[26] C. L. Hewett, *J.*, 1938, 1286; compare H. A. Weidlich, *Ber.*, 1938, **71**, 1203.

It is now recognised that addition of halogens to a double bond is a two-stage process and that the entering halogen atoms arrange themselves as remotely as possible from each other (*trans*-addition). Consequently it is of interest that measurement of the dipole moments of the dichlorides (LXX) has shown that additions of chlorine to 1 : 5-dichloro- and 9 : 10-diphenyl-anthracene are pure *cis*-reactions.[27] The suggestion is made that this may be interpreted as due to primary addition of a chlorine *molecule* rather than chlorine *atoms*, as in the addition of oxygen or maleic anhydride to anthracene and its derivatives (see p. 189). In the case of 1 : 8-dichloroanthracene, however, addition of chlorine is a normal *trans*-reaction, for the dipole moment of the dichloride is smaller than that of the parent compound. Dipole moment measurements of the stereoisomeric diols (LXX; X = OH) formed by hydrolysis of the 1 : 5-dichloroanthracene dihalides are in agreement with the configurations assigned to these diols by E. de B. Barnett, J. W. Cook, and M. A. Matthews.[28]

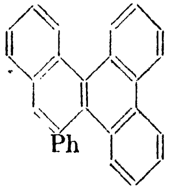
The stereochemistry of the Pschorr phenanthrene synthesis has been studied by P. Ruggli.[29] This synthesis depends for its success on the circumstance that the carboxyl group of *o*-nitro-α-phenylcinnamic acid (LXXI) and its derivatives induces a *cis*-configuration of the two aromatic nuclei. *trans*-*o*-Aminostilbene fails to give phenanthrene, whereas the *cis*-isomeride does so. In fact, the ring-closure of stilbene derivatives to phenanthrenes serves as a criterion for the *cis*-configuration. Similarly F. Bergmann[30] found that both of the stereoisomeric α-(9-phenanthryl)-stilbenes (LXXII) give lithium compounds; but only one of these reacts with carbon dioxide to give 10-phenyl-1 : 2 : 3 : 4-dibenzphenanthrene (LXXIII); the other gives αβ-diphenyl-α-(9-phenanthryl)succinic anhydride.



(LXXI.)



(LXXII.)



(LXXIII.)

Synthesis.

So much of the work on polycyclic aromatic compounds published during the period under review has been devoted to their synthesis that it is impossible to give anything approaching a complete account of this in a comparatively short Report. Much of the earlier work has been summarised by L. F. Fieser,[31] and in the present Report treatment will be confined largely to the more recent publications, and especially to methods and techniques which show novel features.

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[27] E. Bergmann and A. Weizmann, *J. Amer. Chem. Soc.*, 1938, **60**, 1801.

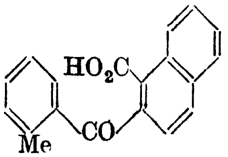
[28] *Rec. Trav. chim.*, 1925, **44**, 728.

[29] P. Ruggli and A. Staub, *Helv. Chim. Acta*, 1936, **19**, 1288; 1937, **20**, 37; P. Ruggli and A. Dinger, *ibid.*, 1941, **24**, 173.

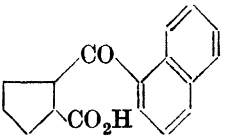
[30] *J. Amer. Chem. Soc.*, 1942, **64**, 69.

[31] "The Chemistry of Natural Products related to Phenanthrene," New York, 1936.

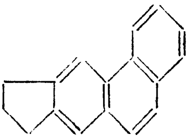
Numerous refinements and modifications have been made to well-known methods for the synthesis of anthracene and phenanthrene derivatives. The interaction of arylmagnesium halides with dicarboxylic anhydrides (*e.g.*, phthalic or succinic anhydride) gives phthaloylic acids or β-aroylpropionic acids in good yield [32] and this reaction has been extensively used for the preparation of intermediates in the synthesis of anthracene or phenanthrene derivatives. For instance, *o*-anisylmagnesium bromide was condensed with phthalic anhydride [33] or *o*-tolylmagnesium bromide with naphthalene-1 : 2-dicarboxylic anhydride.[34] The latter unsymmetrical anhydride gave mainly the keto-acid (LXXIV), from which homologues of 1 : 2-benzanthracene are obtainable. Hydroaromatic keto-acids are likewise formed from phenylmagnesium bromide and Δ^4-tetrahydrophthalic anhydride or from *cis*-hexahydrophthalic anhydride by the Friedel–Crafts reaction.[35] Other examples of interaction of Grignard reagents with phthalic anhydrides are given by R. Bousset,[36] L. F. Fieser and E. B. Hershberg,[37] and by L. F. Fieser and A. M. Seligman.[38] From α-naphthylmagnesium bromide and *cyclo*pentane-1 : 2-dicarboxylic anhydride was obtained a keto-acid (LXXV) which was converted into 2 : 3-*cyclo*pentenophenanthrene (LXXVI).[39] Similarly, condensations between 9-phenanthrylmagnesium bromide and succinic anhydride [40] or αβ-dimethylsuccinic anhydride,[41] and between α- or β-naphthylmagnesium bromide and αβ-dimethylsuccinic anhydride [41] gave keto-acids which were converted into homologues of triphenylene (LXXVII) [42] or phenanthrene.

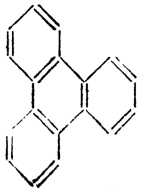


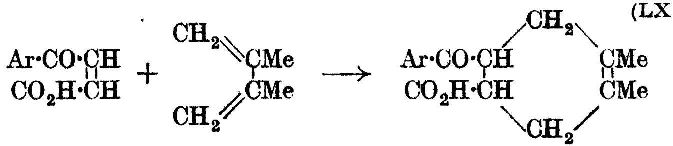
(LXXIV.)



(LXXV.)


(LXXVI.)


(LXXVII.)



(LXXVIII.) (LXXIX.) (LXXX.)

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[32] C. Weizmann, E. Bergmann, and F. Bergmann, *J.*, 1935, 1367; C. Weizmann, O. Blum-Bergmann, and F. Bergmann, *ibid.*, p. 1370; C. Weizmann and E. Bergmann, *J.*, **1936**, 567.

[33] B. P. Geyer, *J. Amer. Chem. Soc.*, 1942, **64**, 2226.

[34] L. F. Fieser and M. S. Newman, *ibid.*, 1936, **58**, 2376.

[35] L. F. Fieser and F. C. Novello, *ibid.*, 1942, **64**, 802.

[36] *Bull. Soc. chim.*, 1935, **2**, 2182.

[37] *J. Amer. Chem. Soc.*, 1937, **59**, 1028. [38] *Ibid.*, 1938, **60**, 170.

[39] E. Bergmann and O. Blum-Bergmann, *ibid.*, 1937, **59**, 1572.

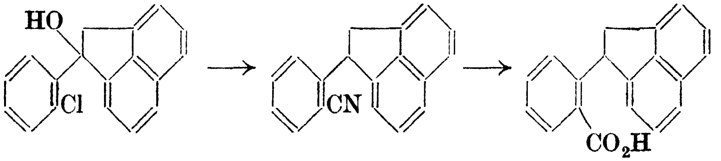
[40] *Idem*, *ibid.*, p. 1441. [41] L. F. Fieser and W. H. Daudt, *ibid.*, 1941, **63**, 782.

[42] See also L. F. Fieser and L. M. Joshel, *ibid.*, 1939, **61**, 2958.

An interesting route to aroylbenzoic acids has been provided by the dehydrogenation with sulphur of compounds of type (LXXX) formed by the Diels–Alder addition of dimethylbutadiene (LXXIX) to β-aroylacrylic acids.[43] The β-aroylacrylic acids (LXXVIII) were obtained from maleic anhydride and aromatic hydrocarbons by the Friedel–Crafts reaction.

The cyclisation of *o*-benzoylbenzoic acids to anthraquinone derivatives * is often difficult to effect and better results may then be obtained by preliminary reduction to *o*-benzylbenzoic acids. For this reduction zinc dust and alkali may frequently be successfully used, but in other cases (*e.g.*, *o*-1-naphthoylbenzoic acid[44]) the yields are poor. In such cases high-pressure hydrogenation over a copper chromite catalyst has been found very effective.[45] The ready dehydration of *o*-benzylbenzoic acid to anthrone[46] is complicated in other cases by sulphonation or by oxidation of the unstable anthranol. In such cases dehydration to anthranyl acetates by acetic anhydride containing hydriodic acid[47] or by acetic acid and acetic anhydride containing zinc chloride[48] gives excellent results.

Another procedure which has been used for the formation of compounds of *o*-benzylbenzoic acid type is illustrated by a synthesis described by L. F. Fieser and J. Cason.[49] *o*-Chlorophenylmagnesium bromide was condensed with acenaphthenone to give a carbinol (LXXXI), which was converted by dehydration and hydrogenation into *o*-chlorophenylacenaphthene. The chlorine in this was replaced by the cyano-group by means of cuprous cyanide, and the product (LXXXII) hydrolysed to the acid (LXXXIII).



(LXXXI.) (LXXXII.) (LXXXIII.)

In a variant of this, 4-methyl-1-naphthylmagnesium bromide was condensed with *o*-chloroacetophenone, and the product transformed through similar

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[43] L. F. Fieser and M. Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 1679.

[44] R. Scholl, C. Seer, and A. Zinke, *Monatsh.*, 1920, **41**, 601.

[45] L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, 1937, **59**, 1028, 2331; L. F. Fieser and H. Heymann, *ibid.*, 1941, **63**, 2333; 1942, **64**, 376.

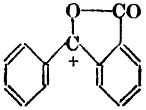
[46] E. de B. Barnett, J. W. Cook, and I. G. Nixon, *J.*, 1927, 508.

[47] R. Scholl and K. Meyer, *Ber.*, 1932, **65**, 1398; R. Scholl, G. von Hornuff, and H. K. Meyer, *Ber.*, 1936, **69**, 707.

[48] L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, 1937, **59**, 1028; compare F. F. Blicke and R. J. Warzynski, *ibid.*, 1940, **62**, 3191.

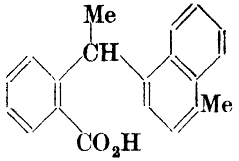
[49] *J. Amer. Chem. Soc.*, 1940, **62**, 432.

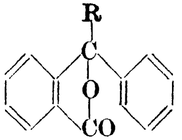
* The mechanism of this dehydration has been studied by M. S. Newman (*J. Amer. Chem. Soc.*, 1942, **64**, 2324), who suggests that the first stage is the formation of a positive carbonium ion:



stages into the acid (LXXXIV).[50] Compounds of this type, which may be converted into *meso*-substituted anthracenes by cyclo-dehydration and then reduction, have been obtained frequently by reduction of the phthalides (type LXXXV) formed by the interaction of Grignard reagents with *o*-benzoylbenzoic acids.[51]

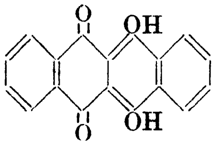
(LXXXIV.)



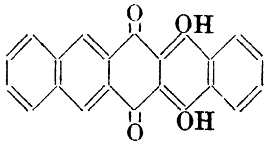


(LXXXV.)

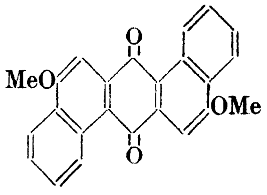
In suitable cases moderately complex structures may be obtained by quite simple procedures. Phthalic acids frequently condense directly with aromatic compounds to give anthraquinones when fused with aluminium chloride–sodium chloride.[52] An alternative condensing agent is boric acid, which effects smooth condensation of 1 : 4-dihydroxynaphthalene with phthalic anhydride or naphthalene-2 : 3-dicarboxylic anhydride to give a dihydroxynaphthacenequinone (LXXXVI) or a dihydroxypentacenequinone (LXXXVII).[53] A monohydroxynaphthacenequinone was obtained from *o*-(1-hydroxy-2-naphthoyl)benzoic acid by the well-known cyclisation with boric acid and sulphuric acid.[54] 3 : 7-Dimethoxy-1 : 2 : 5 : 6-dibenzanthraquinone (LXXXVIII) was obtained by J. Cason and L. F. Fieser [55] by the action of aluminium chloride on 4-methoxy-2-naphthoyl chloride.



(LXXXVI.)



(LXXXVII.)



(LXXXVIII.)

In the dehydration of benzoylbenzoic acids to anthraquinones by acid chlorides at high temperatures,[56] the addition of a few drops of concentrated sulphuric acid is recommended by H. Waldmann.[57]

The Elbs pyrolysis reaction for the synthesis of anthracene hydrocarbons has been used for the production of a wide variety of these.[31] It consists in the thermal dehydration of derivatives of *o*-methylbenzophenone. A modification of this has been introduced successfully by Fieser and his collaborators for the synthesis of 20-methylcholanthrene (VI) and compounds of analogous structure. Thus, the ketone (LXXXIX), obtained from 7-cyano-4-methylindane and α-naphthylmagnesium bromide, gave 20-methylcholanthrene in 50% yield when heated at 405—410° for 40 minutes.[58] Cholanthrene itself [59] and other of its derivatives and analogues [60] have been similarly prepared. The methylene group of a six-membered ring has also been used in place of the methyl group of the earlier examples of the Elbs reaction.[61]

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[50] L. F. Fieser and A. M. Seligman, *J. Amer. Chem. Soc.*, 1939, **61**, 136.

[51] L. F. Fieser and M. S. Newman, *ibid.*, 1936, **58**, 2376; M. S. Newman, *ibid.*, 1937, **59**, 1003; L. F. Fieser and G. W. Kilmer, *ibid.*, 1939, **61**, 862; J. W. Cook, A. M. Robinson, and F. Goulden, *J.*, 1937, 393; A. T. Marchevskiĭ and M. I. Ushakov, *J. Gen. Chem. U.S.S.R.*, 1940, **10**, 1369; B. M. Mikhaĭlov and A. N. Blokhina, *ibid.*, p. 1793.

[52] See, *e.g.*, F. Mayer, O. Stark, and K. Schön, *Ber.*, 1932, **65**, 1336.

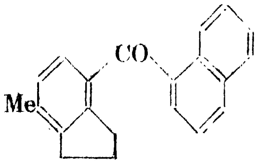
[53] C. Weizmann, L. Haskelberg, and T. Berlin, *J.*, 1939, 398; compare O. Dimroth and R. Fick, *Annalen*, 1916, **411**, 325.

[54] I. Y. Postovskiĭ and L. N. Golyrev, *J. Gen. Chem. U.S.S.R.*, 1941, **11**, 429.

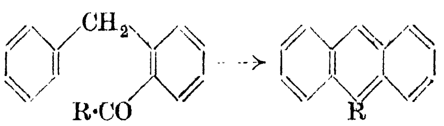
[55] *J. Amer. Chem. Soc.*, 1941, **63**, 1256.

[56] *E.g.*, D.R.-P. 590,579.

[57] *J. pr. Chem.*, 1938, **150**, 121.



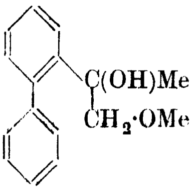
(LXXXIX.)

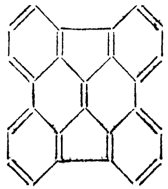


(XC.) (XCI.)

E. Bergmann [62] noted the formation of anthracene in the acid hydrolysis of the acetal of *o*-benzylbenzaldehyde, and this observation was extended by C. K. Bradsher,[63] who obtained 9-alkylanthracenes (XCI) in 70—80% yields by prolonged heating of *o*-benzylphenyl ketones (XC) with hydrogen bromide in acetic acid. This reaction bears considerable resemblance to the Elbs pyrolysis. A somewhat similar method was used for the synthesis of 9- and 9 : 10-substituted phenanthrenes.[64] For example, 9-methylphenanthrene was obtained from the carbinol (XCII) by refluxing with hydrogen bromide in acetic acid. The formation of 2 : 3 : 6 : 7-tetramethoxy-9 : 10-dialkylanthracenes by condensation of veratrole with aliphatic aldehydes is described by A. Müller, M. Raltschewa, and M. Papp;[65] the condensation is accompanied by dehydrogenation of the intermediate dihydroanthracene derivative. V. I. Khmelevskiĭ and G. I. Fedorov [66] obtained 9 : 10-diphenyl-

(XCII.)





(XCIII.)

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[58] L. F. Fieser and A. M. Seligman, *J. Amer. Chem. Soc.*, 1936, **58**, 2482; compare *idem*, *ibid.*, 1935, **57**, 228, 942.

[59] L. F. Fieser and A. M. Seligman, *ibid.*, 1935, **57**, 2174; W. F. Bruce, *ibid.*, 1941, **63**, 301.

[60] L. F. Fieser *et al.*, *ibid.*, 1935, **57**, 1681; 1937, **59**, 394, 883, 2561; 1938, **60**, 176, 2255; 1940, **62**, 2103.

[61] L. F. Fieser and A. M. Seligman, *ibid.*, 1936, **58**, 478.

[62] *J. Org. Chem.*, 1939, **4**, 1.

[63] *J. Amer. Chem. Soc.*, 1940, **62**, 486, 1077.

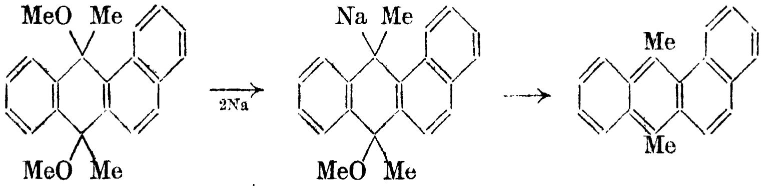
[64] C. K. Bradsher *et al.*, *ibid.*, 1938, **60**, 2960; 1939, **61**, 1524, 2184.

[65] *Ber.*, 1942, **75**, 692.

[66] *J. Gen. Chem. U.S.S.R.*, 1939, **9**, 1423.

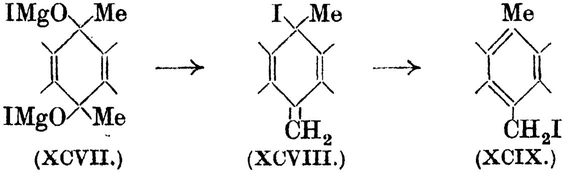
anthracene in 20% yield by heating benzophenone with calcium; similar treatment of fluorenone gave the red hydrocarbon, rubicene (XCIII).

The action of Grignard reagents on anthraquinone furnishes a convenient method of introducing alkyl or aryl substituents into both *meso*-positions of anthracene and its derivatives. On account of the lack of solubility of these quinones in ethyl ether the use of butyl ether has been suggested.[67] With alkyl substituents, direct reduction of the 9 : 10-diols is troublesome; the difficulty has been overcome in a very ingenious manner by W. E. Bachmann and J. M. Chemerda,[68] who converted the diol from 1 : 2-benzanthraquinone and methylmagnesium iodide into its dimethyl ether (XCIV), from which the hydrocarbon (XCVI) was obtained by shaking with powdered sodium in ether–benzene. They interpret the reaction [69] as involving replacement of one methoxy-group by sodium, followed by transannular loss of sodium methoxide from the product (XCV) :



(XCIV.) (XCV.) (XCVI.)

This method gives excellent results and has been used for the synthesis of a number of 9 : 10-dialkylanthracenes.[70] An alternative procedure was described by R. B. Sandin and L. F. Fieser,[71] who obtained an iodomethyl compound (XCIX) (also prepared directly from 9-methyl-1 : 2-benzanthracene) by addition of hydrogen iodide to the magnesium complex (XCVII) from 1 : 2-benzanthraquinone and methylmagnesium iodide. The formation of the iodomethyl compound is believed to take place by isomerisation of the intermediate (XCVIII) and its reduction with stannous chloride was stated to give 9 : 10-dimethyl-1 : 2-benzanthracene (XCVI) in 99% yield!



(XCVII.) (XCVIII.) (XCIX.)

9 : 10-Dialkyl-9 : 10-dihydroanthracenes are formed by the action of alkyl halides on the disodio-addition compound of anthracene [72] and may be dehydrogenated to dialkylanthracenes.[73]

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[67] C. F. H. Allen and R. W. McGibbon, *Canadian J. Res.*, 1938, **16**, *B*, 35.

[68] *J. Amer. Chem. Soc.*, 1938, **60**, 1023. [69] *Ibid.*, 1939, **61**, 2358.

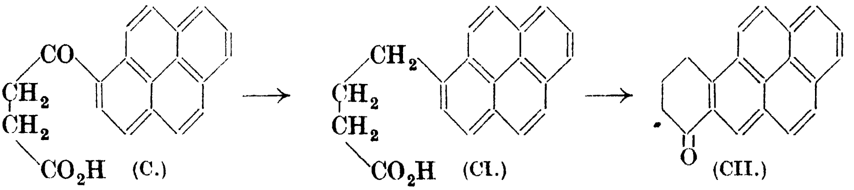
[70] *Idem*, *J. Org. Chem.*, 1939, **4**, 583; 1941, **6**, 36; G. M. Badger, J. W. Cook, and F. Goulden, *J.*, 1940, 16.

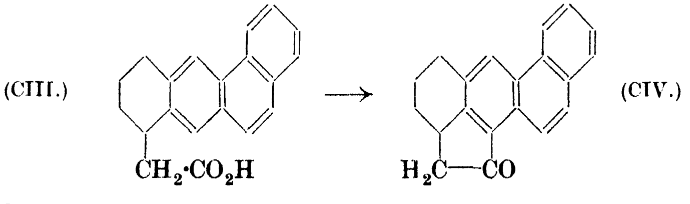
[71] *J. Amer. Chem. Soc.*, 1940, **62**, 3098.

[72] M. Lerer, *Ann. Off. nat. Comb. liq.*, 1933, **8**, 681.

[73] Compare G. Hugel and M. Lerer, *Bull. Soc. chim.*, 1933, **53**, 1497.

One of the most generally useful methods for the synthesis of polycyclic hydrocarbons is that whereby a four-carbon chain is attached, in stages, by its terminal carbon atoms, to *ortho*-positions of an aromatic ring. This leads to fusion of a new six-membered ring, which may be rendered aromatic by dehydrogenation. The simplest procedure for effecting this is the Friedel–Crafts reaction with succinic anhydride, followed by reduction of the β-aroylpropionic acid to a γ-arylbutyric acid and then cyclisation of this. This method was used by R. D. Haworth [74] * for the synthesis of phenanthrene homologues and by J. W. Cook and C. L. Hewett [75] to establish the structure of 3 : 4-benzpyrene (IV), the potent carcinogenic hydrocarbon isolated from coal tar [17 (p. 156)]. The latter synthesis has been improved in several stages by subsequent workers. Reduction of pyrenoylpropionic acid (C) to pyrenylbutyric acid (CI) is suitably carried out by zinc dust and alkali under pressure.[76] Cyclisation of (CI) to ketotetrahydrobenzpyrene (CII) was the least satisfactory stage of the original synthesis. The best method of effecting this is Bachmann's modification [77] of the method of Fieser.[78] This consists in the action of stannic chloride on the chloride of the acid (CI) in cold benzene solution. The pentacyclic ketone is readily obtained pure in almost theoretical yield and the same procedure has given excellent results in the cyclisation of many other arylbutyric acids (Fieser, Bachmann) and also in such cases as the cyclisation of the acid (CIII) to the cholanthrene derivative (CIV).[79]





Reduction of the carbonyl group of (CII) is necessary before dehydrogenation to benzpyrene, if satisfactory yields are to be obtained, and this may be effected suitably by high-pressure hydrogenation with copper chromite (which gives tetrahydrobenzpyrene)[80] or by aluminium *iso*propoxide.[77] The latter method gives the carbinol, which is readily dehydrated to dihydrobenzpyrene. Many other examples have been given of the reduction of ketones of type (CII) by aluminium *iso*propoxide.

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[74] *J.*, 1932, 1125. [75] *J.*, 1933, 398.

[76] H. Vollmann *et al.*, *Annalen*, 1937, **531**, 128.

[77] W. E. Bachmann, M. Carmack, and S. R. Safir, *J. Amer. Chem. Soc.*, 1941, **63**, 1684.

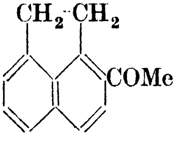
[78] L. F. Fieser and F. C. Novello, *ibid.*, 1940, **62**, 1858.

[79] W. E. Bachmann, *J. Org. Chem.*, 1938, **3**, 434.

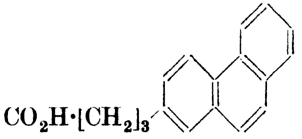
* E. Mosettig and H. M. Duvall (*J. Amer. Chem. Soc.*, 1937, **59**, 367) found a convenient route to 1- and 4-phenanthrol in the palladium dehydrogenation of Haworth's ketotetrahydrophenanthrenes.

Another excellent reagent for bringing about the cyclisation of acids of type (CI) is anhydrous hydrogen fluoride, which is commercially available in the United States and has been extensively used by Fieser and his school, not only for cyclisations but also as a condensing agent in Friedel–Crafts reactions,[81] for which, however, the method is not of general application. J. H. Simons, S. Archer, *et al.*[82] had already carried out a series of alkylations with hydrogen fluoride,* which was also used by W. S. Calcott, J. M. Tinker, and V. Weinmayr [83] for the synthesis of perylene (XLV) from phenanthrene and acraldehyde, and of 4 : 5-benzpyrene (CXII) from 9 : 10-dihydroanthracene and acraldehyde.

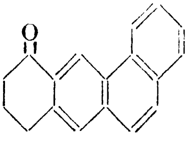
The use of hydrogen fluoride sometimes alters the course of a reaction. Acenaphthene and acetic acid reacted with hydrogen fluoride to give 94% of a mixture of acetylacenaphthenes, from which 25% was easily isolated as the hitherto relatively inaccessible 1-acetylacenaphthene (CV).[81] Moreover, in the cyclisation of γ-(2-phenanthryl)butyric acid (CVI) L. F. Fieser and W. S. Johnson [84] obtained a 78% yield of the ketotetrahydrobenzanthracene (CVII) with hydrogen fluoride, whereas the ketotetrahydrochrysene (CVIII) was mainly found when the acid (CVI) was cyclised with 85% sulphuric acid.[14]



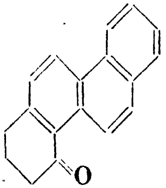
(CV.)



(CVI.)



(CVII.)



(CVIII.)

Cyclisation of γ-(3-phenanthryl)butyric acid (LV) with hydrogen fluoride does not appear to have been described. It would be of interest to know if this occurs in position 4 (cf. p. 171).

The succinic anhydride condensation (by the Friedel–Crafts or the Grignard reaction) is by no means the only method by which the four-carbon chain may be introduced in syntheses of the type discussed above. An acetyl or other acyl substituent may be brominated, and the product condensed with malonic ester derivatives; alternatively the carbonyl group may be condensed with ethyl succinate, or reduced to carbinol with aluminium *iso*propoxide,[85] then the hydroxyl replaced by chlorine, and the chloro-compound condensed with malonic ester derivatives; the latter procedure gives a three-carbon chain terminating in carboxyl, and this may be extended by the Arndt–Eistert reaction. In all these ways suitably substituted four-carbon chains have been attached to aromatic molecules, and further substituents may be introduced by the action of Grignard reagents on aroylpropionic acids or the ketotetrahydo-compounds obtained by cyclisation of arylbutyric acids. Reactions such as these have been used for the synthesis of a wide variety of derivatives of phenanthrene, chrysene (CXXXIV), 1 : 2-benzanthracene, triphenylene (LXXVII), and other polycyclic aromatic compounds.

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[80] L. F. Fieser and M. Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 782.

[81] See, *e.g.*, L. F. Fieser and E. B. Hershberg, *ibid.*, 1939, **61**, 1272; 1940, **62**, 49.

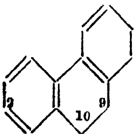
[82] *Ibid.*, 1938, **60**, 986, 2952, 2953, 2955, 2956.

[83] *Ibid.*, 1939, **61**, 949.

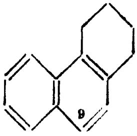
[84] *Ibid.*, p. 1647.

* J. H. Simons (*Ind. Eng. Chem.*, 1940, **32**, 178) gives a review of the uses of hydrogen fluoride in organic chemistry.

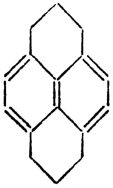
The positions of attachment of the new ring may often be modified by using partially hydrogenated aromatic compounds for the initial condensations. Thus, although phenanthrene is substituted mainly in position 3 and to a lesser extent in position 2, in Friedel–Crafts reactions carried out in nitrobenzene solutions, if 9 : 10-dihydrophenanthrene (CIX) is used, substitution takes place almost exclusively in position 2.[86] As dihydrophenanthrene is readily obtained from phenanthrene by hydrogenation with copper chromite,[87] the scope of this synthetic method becomes very much enlarged. In Friedel–Crafts reactions with 1 : 2 : 3 : 4-tetrahydrophenanthrene (CX) the acyl group enters the 9-position [88] and the succinic anhydride condensation with *s*-hexahydropyrene (CXI) was used by Cook and Hewett [75] for the synthesis of 4 : 5-benzpyrene (CXII).



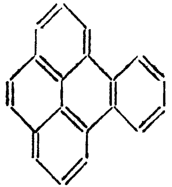
(CIX.)



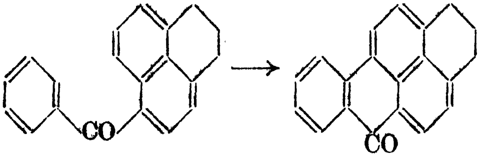
(CX.)



(CXI.)



(CXII.)



(CXIII.) (CXIV.)

A new synthesis of 3 : 4-benzpyrene and its derivatives was developed by L. F. Fieser and E. B. Hershberg,[89] who obtained the keto-compound

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[85] Compare H. Lund, *Ber.*, 1937, **70**, 1520.

[86] A. Burger and E. Mosettig, *J. Amer. Chem. Soc.*, 1935, **57**, 2731; 1936, **58**, 1857; 1937, **59**, 1302.

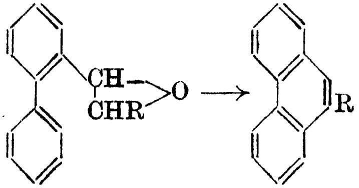
[87] *Idem, ibid.*, 1935, **57**, 2731; J. R. Durland and H. Adkins, *ibid.*, 1937, **59**, 135; L. F. Fieser and W. S. Johnson, *ibid.*, 1939, **61**, 169.

[88] W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, 1939, **4**, 472.

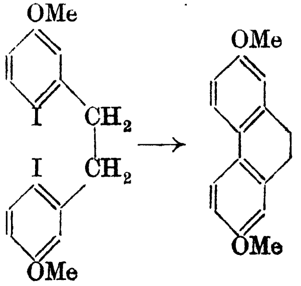
[89] *J. Amer. Chem. Soc.*, 1938, **60**, 1658.

(CXIV) by aluminium chloride–sodium chloride fusion of 3-benzoylperinaphthane (CXIII). The latter was the product of the Friedel–Crafts reaction between benzoyl chloride and perinaphthane, which was formed by copper chromite hydrogenation of perinaphthenone (XXXV; R = H).

9-Alkylphenanthrenes (CXVI) were obtained by C. K. Bradsher and S. T. Amore[90] by the action of hydrogen bromide in acetic acid on oxides of the type (CXV), synthesised from *o*-iododiphenyl. J. W. Cornforth and (Sir) R. Robinson[91] obtained 2 : 7-dimethoxy-9 : 10-dihydrophenanthrene (CXVIII) by heating 6 : 6′-di-iodo-3 : 3′-dimethoxydibenzyl (CXVII) with copper bronze. This dibenzyl derivative (CXVII) was readily synthesised from *m*-methoxybenzyl chloride. T. Hasselstrom[92] found a suitable method for the preparation of 1-methylphenanthrene in quantity, in the thermal degradation of retene (1-methyl-7-*iso*propylphenanthrene) by 9 hours' boiling in contact with fuller's earth.



(CXV.) (CXVI.)



(CXVII.) (CXVIII.)

The Pschorr phenanthrene synthesis continues to provide a valuable method in many instances, and within recent years has been used for the preparation of various homologues and derivatives of phenanthrene[93] and of 4 : 5-methylenedioxychrysene,[94] 1 : 2-dimethylchrysene (XI),[95] 1 : 2 : 7 : 8-dibenzanthracene,[96] 3 : 4 : 5 : 6-dibenzphenanthrene (LXVI),[25] 1 : 2 : 3 : 4-dibenzphenanthrene (X),[97] picene,[98] and cholanthrene.[99]

The synthesis of derivatives of 3 : 4-benzphenanthrene has received attention on account of the carcinogenic properties of some members of this group. The most generally useful method is that of C. L. Hewett.[1] This is based on a patented method for synthesising phenanthrene derivatives.[2] Elimination of hydrogen bromide from the acid (CXIX) by fusion with potash leads to 3 : 4-benz-1-phenanthroic acid (CXX) in 60% yield. The method lends itself to considerable variation. Other benzphenanthrene syntheses of less general application have also been described.[3] The benzretene obtained from retene by the succinic anhydride synthesis by D. E. Adelson and M. T. Bogert[4] was originally thought to be a 3 : 4-benzphenanthrene derivative, but was afterwards shown to be a homologue of 1 : 2-benzanthracene.[5]

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[90] *J. Amer. Chem. Soc.*, 1941, **63**, 493; compare *ibid.*, 1939, **61**, 3131; 1940, **62**, 2806.

[91] *J.*, 1942, 684.

[92] *J. Amer. Chem. Soc.*, 1941, **63**, 1164.

[93] M. T. Bogert and G. S. Stamatoff, *Rec. Trav. chim.*, 1933, **52**, 584; J. T. Cassaday and M. T. Bogert, *J. Amer. Chem. Soc.*, 1939, **61**, 2461, 3055; R. A. Konovalova, S. Junusov, and A. P. Orékhov, *J. Gen. Chem. U.S.S.R.*, 1939, **9**, 1507; *Bull. Soc. chim.*, 1939, **6**, 1479; E. E. Lewis and R. C. Elderfield, *J. Org. Chem.*, 1940, **5**, 290; T. M. Sharp, *J.*, 1936, 1234; P. Hill and W. F. Short, *J.*, 1937, 260; A. Higginbottom, P. Hill, and W. F. Short, *ibid.*, p. 263; C. L. Hewett and R. H. Martin, *J.*, 1940, 1396.

[94] L. H. Briggs and J. M. Wilson, *J.*, 1941, 500.

[95] C. L. Hewett, *J.*, 1940, 293.

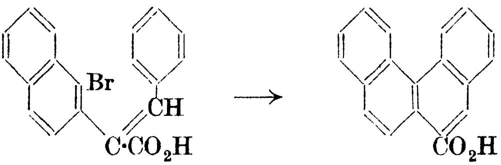
[96] J. W. Cook, *J.*, 1932, 1472.

[97] C. L. Hewett, *J.*, 1938, 193.

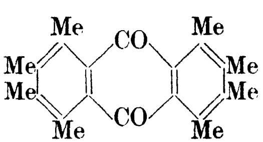
[98] H. Waldmann and G. Pitschak, *Annalen*, 1937, **527**, 183.

[99] L. F. Fieser and G. W. Kilmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1354.

[1] *J.*, 1938, 1286; 1940, 293, 1159.



(CXIX.) (CXX.)



(CXXI.)

The Diels–Alder diene synthesis continues to be used to build up polycyclic structures.* The formation of hydroanthraquinones from conjugated dienes and *p*-benzoquinone or α-naphthaquinone was among the earliest examples of this reaction; more recently, H. J. Backer, J. Strating, and L. H. H. Huisman[6] obtained octamethylanthraquinone (CXXI) by aerial oxidation of the adduct of αβγδ-tetramethylbutadiene and *p*-benzoquinone. Other fully substituted anthraquinones were similarly prepared, as well as the corresponding anthracene hydrocarbons. From hexatriene and α-naphthaquinone, 1-vinylanthraquinone was prepared.[7] By addition of maleic anhydride to dienes of the type (CXXII), H. A. Weidlich[8] obtained anhydrides such as (CXXIII), from which were prepared by decarboxylation and dehydrogenation, 1 : 2 : 5 : 6- and 3 : 4 : 5 : 6-dibenzphenanthrene (LXVI), 1 : 12-benzperylene (I) and picene. E. Clar[9] prepared a series of polycyclic compounds by addition of methyleneanthrone (CXXIV) to maleic anhydride, cinnamic acid and various 1 : 4-quinones. A new type of diene synthesis was described by K. Alder and H. F. Rickert,[10] who found that under forced conditions, and in the presence of an inhibitor of polymerisation, styrene will combine with butadiene and other conjugated dienes. Similarly, indene

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[2] I.G., *Brit. Pat.* 469,633.

[3] See, *e.g.*, C. L. Hewett, *J.*, 1936, 596; M. S. Newman and L. M. Joshel, *J. Amer. Chem. Soc.*, 1938, **60**, 485; 1940, **62**, 972; W. E. Bachmann and R. O. Edgerton, *ibid.*, p. 2970; N. C. Ganguly, *Science and Culture*, 1941, **7**, 320.

[4] *J. Amer. Chem. Soc.*, 1937, **59**, 1776.

[5] L. F. Fieser and R. C. Clapp, *ibid.*, 1941, **63**, 319.

[6] *Rec. Trav. chim.*, 1939, **58**, 761.

[7] L. W. Butz, E. W. J. Butz, and A. M. Gaddis, *J. Org. Chem.*, 1940, **5**, 171.

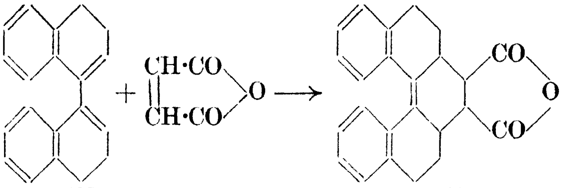
[8] *Ber.*, 1938, **71**, 1203.

[9] *Ber.*, 1936, **69**, 1686; see also C. F. H. Allen *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 656.

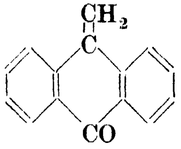
[10] *Ber.*, 1938, **71**, 379.

* For a general review of the Diels–Alder diene synthesis, see J. A. Norton, *Chem. Reviews*, 1942, **31**, 319.

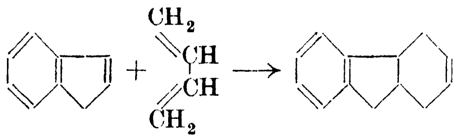
(CXXV) and butadiene combine to give a tetrahydrofluorene (CXXVI), from which fluorene may be obtained by dehydrogenation with selenium. Indene has also been condensed with methyleneanthrone (CXXIV) to give a product which was dehydrogenated to the *meso*-benzanthrone derivative (CXXVII).[11]



(CXXII.) (CXXIII.)

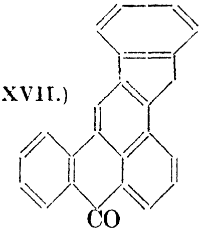


(CXXIV.)



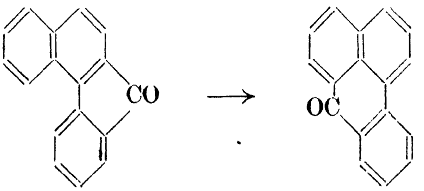
(CXXV.) (CXXVI.)

(CXXVII.)



Fluorene derivatives have also been prepared from α-hydrindone by the Mannich reaction[12] and the structural relationships of the dibenzfluorenes have been clarified by the synthetic work of R. H. Martin[13] and G. Swain and A. R. Todd.[14] The chemistry of fluorene and its derivatives has been reviewed by G. Rieveschl and F. E. Ray.[15] New methods of passage from the fluorene series to the phenanthrene series have been described. R. F. Schultz, E. D. Schultz, and J. Cochran[16] obtained 9-phenanthrol and (principally) its methyl ether by ring-enlargement of fluorenone with diazomethane, and W. G. Brown and B. Bluestein[17] obtained phenanthrene in almost quantitative yield by dehydration of 9-fluorenylcarbinol. F. G. Baddar[18] converted 3 : 4-benzfluorenone (CXXVIII) into *meso*-benzanthrone (CXXIX) by fusion with aluminium chloride–sodium chloride.

(CXXVIII.)



(CXXIX.)

New syntheses of chysene derivatives have been described.[19]

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[11] G. Swain and A. R. Todd, *J.*, 1942, 626.

[12] R. H. Harradence and F. Lions, *J. Proc. Roy. Soc. N.S.W.*, 1939, **72**, 284.

[13] *J.*, 1941, 679.

[14] *Ibid.*, p. 674.

[15] *Chem. Reviews*, 1938, **23**, 287.

[16] *J. Amer. Chem. Soc.*, 1940, **62**, 2902.

[17] *Ibid.*, p. 3256.

[18] *J.*, 1941, 310.

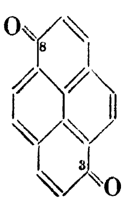
[19] M. S. Newman, *J. Amer. Chem. Soc.*, 1938, **60**, 2947; 1940, **62**, 870, 2295; C. K. Bradsher and A. S. Burhans, *ibid.*, 1940, **62**, 3140; L. M. Joshel, L. W. Butz, and J. Feldman, *ibid.*, 1941, **63**, 3348; L. W. Butz and L. M. Joshel, *ibid.*, 1942, **64**, 1311.

Reactions.

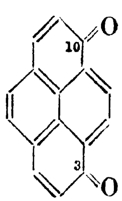
This section will be devoted chiefly to the reactions of the anthracene group, which show many features of unusual interest. Reactions of other classes of polycyclic compounds have been extensively studied, but are for the most part the normal reactions of aromatic compounds. Their interest lies partly in the products which may be obtained thereby, and in the positions at which substitution occurs.

Substituents may be introduced directly into four of the five positions of phenanthrene by suitable procedures. The 1-, 2-, 3- and 9-aldehydes have all been obtained from the carboxylic acids.[20] The oximes of 1-, 2-, 3- and 9-acetylphenanthrenes give almost exclusively the acetamido-compounds by the Beckmann rearrangement; the oximes of the benzoyl-phenanthrenes give in addition anilides of the corresponding acids (these are the chief products with the 1- and the 9-isomeride). Bachmann and Boatner,[20] who carried out these transformations, diazotised the 1-, 2- and 3-aminophenanthrenes by the procedure of C. de Milt and G. van Zandt[21] for the diazotisation of weakly basic and insoluble amines. They prepared by this means the 1-, 2- and 3-chloro-, -bromo- and -iodo-phenanthrenes. The kinetics of the addition of bromine to phenanthrene have been studied by C. C. Price.[22] A. Jeanes and R. Adams[23] have shown that alkali metals add on to phenanthrene only at the 9 : 10 positions,[24] which are also the positions attacked in the oxidation of phenanthrene by osmium tetroxide.[25]

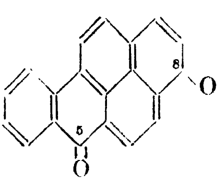
A comprehensive survey of the chemistry of pyrene (XXVIII) by H. Vollmann, H. Becker, M. Corell, and H. Streeck[64 (p. 163)] has elucidated the positions of substitution in numerous reactions and has disclosed methods for the introduction of substituents into the positions (1, 1 : 2, 1 : 6) not directly attacked. Oxidation of pyrene with chromic acid gave a mixture of 3 : 8- and 3 : 10-quinones (CXXX and CXXXI), which were separated, and their structures determined. Oxidation of 3 : 4-benzpyrene likewise gave a mixture of quinones (CXXXII and CXXXIII), which Vollmann separated by crystallisation of the products of reductive acetylation. Other reactions



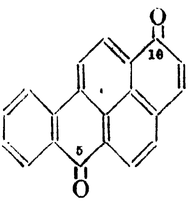
(CXXX.)



(CXXXI.)



(CXXXII.)



(CXXXIII.)

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[20] C. W. Shoppee, *J.*, 1933, 37; W. E. Bachmann, *J. Amer. Chem. Soc.*, 1935, **57**, 555; W. E. Bachmann and C. H. Boatner, *ibid.*, 1936, **58**, 2097.

[21] *Ibid.*, 1936, **58**, 2044.

[22] *Ibid.*, 1936, **58**, 1834, 2101; compare L. F. Fieser and C. C. Price, *ibid.*, p. 1838, and M. S. Kharasch, P. C. White, and F. R. Mayo, *J. Org. Chem.*, 1938, **2**, 574.

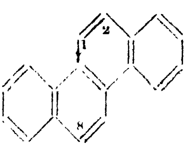
[23] *J. Amer. Chem. Soc.*, 1937, **59**, 2608.

[24] Compare W. Hückel and H. Bretschneider, *Annalen*, 1939, **540**, 157.

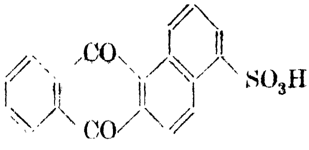
[25] R. Criegee, B. Marchand, and H. Wannowius, *Annalen*, 1942, **550**, 99.

with 3 : 4-benzpyrene led to monosubstitution at position 5 in all cases (nitration, chlorination, oxidation with lead tetra-acetate, diazo-coupling, condensation with *N*-methylformanilide) except in the Friedel–Crafts reaction with acetyl chloride, which gave mainly 10-acetyl-3 : 4-benzpyrene.[26]

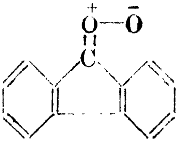
Progress has also been made in the orientation of chrysene derivatives. In monosubstitution the group normally enters the 2-position (CXXXIV). This is the case with chlorination and bromination, nitration, sulphonation, and in the Friedel–Crafts reaction with acetyl and benzoyl chlorides. The various derivatives have been correlated with one another, and with synthetic 2-chrysenol of proved structure.[27] A second product of the Friedel–Crafts reaction with acetyl chloride was shown not to be the 1-acetyl compound, as it was reduced to an ethylchrysene which differed from synthetic 1-ethylchrysene.[27] Disubstitution of chrysene is generally assumed to give symmetrical (2 : 8-) derivatives, but this does not appear to have been rigidly proved.[28] The increasing availability of chrysene, pyrene and fluoranthene (III) has been responsible for a steady increase in the number of patent specifications dealing with substitution products of these hydrocarbons. R. R. Pritchard and J. L. Simonsen [29] showed that sulphonation of *meso*-benzanthrone (XXXI) occurs mainly in position 6, although other substituents chiefly enter the 1′-position. Sulphonation of 1 : 2-benzanthraquinone gives the 4′-sulphonic acid (CXXXV), the structure of which was shown by alkaline fusion to 5-hydroxy-2-naphthoic acid.[30] The oxidation of pyrene and 1 : 2-benzanthracene to quinones by hydrogen peroxide has been recorded,[31] whereas fluorenone was oxidised by hydrogen peroxide in ether to a peroxide to which formula (CXXXVI) is ascribed.[32] Fluorenone reacts with formamide to give the formyl derivative of 9-aminofluorene.[33]



(CXXXIV.)



(CXXXV.)



(CXXXVI.)

Probably the most outstanding reaction which has been found in the anthracene group is the photo-chemical oxidation to transannular peroxides. This appears to be a general reaction of anthracene derivatives, and is not shown by any other group of polycyclic aromatic compounds. The recognition of this resulted from the elucidation of the naphthacene structure of the rubrenes, which were well known to have the capacity to form photo-oxides [2 (p. 156)]. The formation and properties of these "photo-oxides" have been reviewed by C. Dufraisse [34] and also by W. Bergmann and M. McLean [35] in a section of a general article on transannular peroxides.

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[26] A. Windaus and S. Rennhak, *Z. physiol. Chem.*, 1937, **249**, 256; A. Windaus and K. Raichle, *Annalen*, 1939, **537**, 151; L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, 1938, **60**, 2542; 1939, **61**, 1565; H. J. Eckhardt, *Ber.*, 1940, **73**, 15.

[27] K. Funke and E. Müller, *J. pr. Chem.*, 1936, **144**, 242; M. S. Newman and J. A. Cathcart, *J. Org. Chem.*, 1940, **5**, 618.

[28] See K. Funke, E. Müller, and L. Vadasz, *J. pr. Chem.*, 1936, **144**, 265; K. Funke and J. Ristic, *ibid.*, **145**, 309; **146**, 151.

[29] *J.*, 1938, 2047.

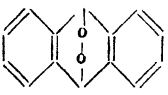
[30] A. Sempronj, *Gazzetta*, 1939, **69**, 448; J. Cason and L. F. Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 2681.

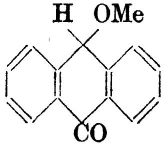
[31] R. T. Arnold and R. Larson, *J. Org. Chem.*, 1940, **5**, 250.

[32] G. Wittig and G. Pieper, *Ber.*, 1940, **73**, 295.

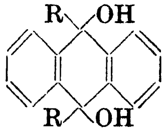
[33] H. Schiedt, *J. pr. Chem.*, 1941, **157**, 203.

Anthracene itself undergoes photo-oxidation, a fact which eluded discovery until 1935.[36, 38] This is remarkable in view of the large number of investigations which had been made on the photo-polymerisation of anthracene. The failure to observe the phenomenon earlier is due in part to the instability of this photo-oxide (CXXXVII), which is completely destroyed by prolonged irradiation, and in part to the circumstances that the photo-polymerisation has been studied mostly in benzene solution, which favours polymerisation but not oxidation. Carbon disulphide is the solvent most favourable for photo-oxidation.[37] Solutions of anthracene in carbon disulphide are non-fluorescent, and loss of fluorescence is concomitant with an increase in the velocity of photo-oxidation. The photo-polymeride of anthracene is not an intermediate in the photo-oxidation, although there are grounds for the belief that partial photo-dimerisation may be involved. A trimeric formula has been suggested for the photo-polymeride of anthracene,[38] the formation of which has been studied from the magnetic standpoint.[39] Anthracene photo-oxide (CXXXVII) liberates iodine from potassium iodide, and is transformed by hydrogen chloride into chloroanthrone, from which the more stable methoxyanthrone (CXXXVIII) was prepared for identification.[38]


(CXXXVII.)



(CXXXVIII.)



(CXXXIX.)

A feature of the rubrene photo-oxides is their ability to undergo thermal dissociation with liberation of oxygen. Similar behaviour is shown by the photo-oxides of 9 : 10-diarylanthracenes, which in favourable cases may liberate up to 95% of their combined oxygen.[40] 10-Aryl-9-alkylanthracene photo-oxides liberated less than 50% of their oxygen on thermal decomposition,[41] whereas 9-alkyl- and 9 : 10-dialkyl-anthracene photo-oxides did not liberate oxygen.[42]

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[34] *Bull. Soc. chim.*, 1939, **6**, 422.

[35] *Chem. Reviews*, 1941, **28**, 367.

[36] C. Dufraisse and M. Gérard, *Compt. rend.*, 1935, **201**, 428; 1936, **202**, 1859.

[37] C. Dufraisse and M. Badoche, *ibid.*, 1935, **200**, 1103.

[38] C. Dufraisse and M. Gérard, *Bull. Soc. chim.*, 1937, **4**, 2052.

[39] S. S. Bhatnagar, P. L. Kapur, and G. Kaur, *Proc. Indian Acad. Sci.*, 1939, **10**, *A*, 468; compare J. Farquarson and M. V. C. Sastri, *Current Science*, 1940, **9**, 135.

[40] C. Dufraisse and A. Étienne, *Compt. rend.*, 1935, **201**, 280; C. Dufraisse and J. le Bras, *Bull. Soc. chim.*, 1937, **4**, 349; D. Duveen and A. Willemart, *J.*, 1939, 116.

meso-Substituents favour the formation of photo-oxides, and although the experiments of Dufraisse and his collaborators were usually carried out in sunlight, they state that, if the solvent is favourable, the ordinary illumination of the laboratory is sufficient. J. W. Cook and R. H. Martin [43] carried out the photo-oxidation of a number of *meso*-substituted 1 : 2-benzanthracenes with the aid of an ordinary gas-filled electric lamp. The ease with which 9 : 10-dimethyl-1 : 2-benzanthracene is photo-oxidised is shown by the fact that Sandin and Fieser [71 (p. 179)] isolated its photo-oxide when they attempted to purify the hydrocarbon by chromatographic means. 9 : 10-Dimethoxyanthracene was the most easily photo-oxidised substance studied by Dufraisse; [44] its solutions are oxidised exceedingly rapidly when exposed to light, but are unaffected in the dark. The sodium salt of anthraquinol is oxidised in the dark, but gives no peroxide. The photo-oxides differ considerably in stability, and the compound from 1 : 4-dimethoxy-9 : 10-diphenylanthracene liberates oxygen even in the cold.[45] The influence of methoxy-groups in various positions was studied by C. Dufraisse and L. Velluz.[46]

The ready elimination of oxygen from these photo-oxides would suggest that they may be molecular compounds. The heat of formation is too great for this, however, although the heat of formation of the photo-oxide of rubrene (L), 22·6 kg.-cals., is small in comparison with that associated with the formation of a stable oxide.[47] The structure of these compounds as *meso*-peroxides is fairly conclusively established by their hydrogenation to derivatives of 9 : 10-dihydroxy-9 : 10-dihydroanthracene (CXXXIX).[48,43]

The mechanism of photo-oxidation was discussed by Dufraisse,[34] who rejects the view that the chief function of light is to induce dissociation to a free radical. If this were so, all *meso*-additions to anthracene derivatives would be activated by light, which is not the case. C. K. Ingold and P. G. Marshall [49] observed that 9 : 10-diarylanthracenes undergo reversible deepening in colour when heated * and attributed this to di-radical formation. C. Dufraisse and J. Houpillart [50] disputed this interpretation and showed that the increase in colour is due to the well-known effect of increase in absorption power with rise in temperature. All attempts to bring about the formation of photo-peroxides in the phenanthrene, naphthalene and acridine series have been unsuccessful,[51] and the phenomenon appears specific to the anthracene series. A. von Rebay and H. Fettback [52] obtained a peroxide of cymene by the direct action of oxygen, but this is an acidic peroxide, and therefore is not analogous to the anthracene photo-oxides.

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[41] A. Willemart, *Compt. rend.*, 1936, **203**, 1372; *Bull. Soc. chim.*, 1939, **6**, 204.

[42] A. Willemart, *Compt. rend.*, 1937, **205**, 866; *Bull. Soc. chim.*, 1938, **5**, 556.

[43] *J.*, 1940, 1125.

[44] C. Dufraisse and R. Priou, *Bull. Soc. chim.*, 1939, **6**, 1649.

[45] C. Dufraisse, L. Velluz, and L. Velluz, *Compt. rend.*, 1939, **208**, 1822; **209**, 516.

[46] *Ibid.*, 1941, **212**, 270.

[47] C. Dufraisse and L. Enderlin, *ibid.*, 1930, **191**, 1321.

[48] C. Dufraisse and J. Houpillart, *ibid.*, 1937, **205**, 740.

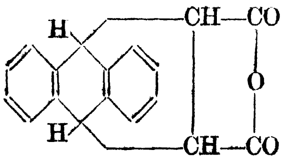
[49] *J.*, 1926, 3080.

[50] *Bull. Soc. chim.*, 1938, **5**, 1628.

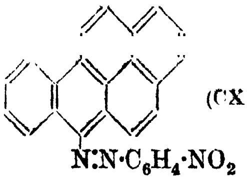
* Some 9 : 10-dialkylanthracenes behave in the same way.—Reporter.

A reaction of anthracenes which has many points of resemblance to photo-oxidation is the Diels–Alder reaction, in which anthracene derivatives participate as diene components, undergoing transannular addition of reagents such as maleic anhydride and its derivatives,[53] *p*-benzoquinone,[54] acetylenedicarboxylic ester,[55] diazoacetic ester,[56] acraldehyde,[57] and even, at somewhat high temperatures, of allyl chloride [58] and vinyl acetate.[59] The reaction with maleic anhydride has been most widely studied. The addition compounds (type CXL) undergo dissociation at high temperatures, and W. E. Bachmann and M. C. Kloetzel [60] demonstrated conclusively that the addition of maleic anhydride is an equilibrium reaction. In the cases of anthracene and its 9-methyl and 9 : 10-dimethyl derivatives the equilibrium was very strongly in favour of the adduct (98—99% formed); in other cases comparatively little combination took place when molecular proportions were used, but satisfactory yields of adduct were formed by using 30 molecular proportions of maleic anhydride. In this way the yields of product were increased as follows: 9 : 10-diphenylanthracene (16% to 78%); 1 : 2 : 5 : 6-dibenzanthracene (30% to 91%); 20-methylcholanthrene (22% to 83%). The rates of reaction varied greatly; 9 : 10-dimethylanthracene reacted rapidly at room temperature, whereas with 9 : 10-diphenylanthracene the reaction was incomplete after days of boiling equimolecular proportions of the reactants in benzene solution. For the steric effects shown by some of these addition compounds, see p. 169.

(CXL.)



(CXLI.)



The high chemical reactivity of many anthracene hydrocarbons has been demonstrated by several substitution reactions investigated in detail by

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[51] C. Dufraisse and R. Priou, *Bull. Soc. chim.*, 1938, **5**, 611; C. Dufraisse and J. Houpillart, *ibid.*, p. 626.

[52] *Ber.*, 1939, **72**, 1643.

[53] O. Diels and K. Alder, *Annalen*, 1931, **486**, 191; E. Clar, *Ber.*, 1931, **64**, 2194.

[54] E. Clar, *Ber.*, 1931, **64**, 1676.

[55] O. Diels and K. Alder, *loc. cit.*; O. Diels and W. Friedrichsen, *Annalen*, 1934, **513**, 145; O. Diels and W. E. Thiele, *Ber.*, 1938, **71**, 1173.

[56] O. Diels, S. Schmidt, and W. Witte, *Ber.*, 1938, **71**, 1186.

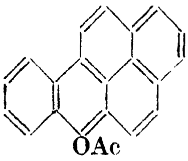
[57] A. G. Slobodskoĭ and V. I. Khmelevskiĭ, *J. Gen. Chem. U.S.S.R.*, 1940, **10**, 1199.

[58] K. Alder and E. Windemuth, *Ber.*, 1938, **71**, 1942.

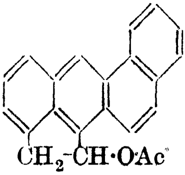
[59] K. Alder and H. F. Rickert, *Annalen*, 1939, **543**, 1.

[60] *J. Amer. Chem. Soc.*, 1938, **60**, 481.

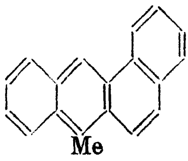
L. F. Fieser and his collaborators. The most striking of these is diazo-coupling, which occurs very readily in certain cases.[61] Both 3 : 4-benzpyrene (IV) and 20-methylcholanthrene (VI) gave deep red colours with *p*-nitrobenzenediazonium chloride, and in the case of benzpyrene the crystalline azo-compound (CXLI) was isolated and its orientation determined.[62] The aldehyde group was directly introduced into the 9- and the 10-position of anthracene and 1 : 2-benzanthracene respectively, by means of *N*-methylformanilide and phosphorus oxychloride. This reaction is not specific to anthracene derivatives, for it is shown also by pyrene[64 (p. 168)] and, slowly, by acenaphthene.[63] 3 : 4-Benzpyrene, 20-methylcholanthrene and certain other anthracene hydrocarbons undergo direct thiocyanation,[64] and they are readily oxidised by lead tetra-acetate. In the case of benzpyrene the 5-acetate (CXLII) is formed in high yield, whereas 20-methylcholanthrene is oxidised in the five-membered ring, giving a mixture of the 15-acetate (CXLIII) and the corresponding 15-keto-compound.[74 (p. 165)]. With 10-methyl-1 : 2-benzanthracene (CXLIV) oxidation takes place in the methyl group in



(CXLII.)



(CXLIII.)



(CXLIV.)

spite of the presence of an unsubstituted (but hindered) *meso*-position. The reaction of chloromethylation, while by no means specific to the anthracene group, takes place very easily with 1 : 2-benzanthracene[65] and gives the 10-chloromethyl derivative.

Despite the length of this Report some of the topics have been treated very superficially, and it has been necessary to omit reference to much important work which comes within the scope and period of this review.

J. W. C.

6. HETEROCYCLIC COMPOUNDS.

Oxygen Ring Compounds.

Flavan Derivatives.—The Simonis synthesis of flavanones from polyhydric phenols and cinnamoyl chloride has been improved;[1] and with cold alcoholic sodium ethoxide the initial isomerisation proceeds quantitatively[2] in the flavone synthesis :

---

[61] L. F. Fieser and W. P. Campbell, *J. Amer. Chem. Soc.*, 1938, **60**, 1142.

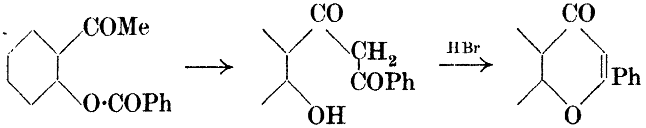
[62] L. F. Fieser and E. B. Hershberg, *ibid.*, 1939, **61**, 1565.

[63] L. F. Fieser and J. E. Jones, *ibid.*, 1942, **64**, 1666.

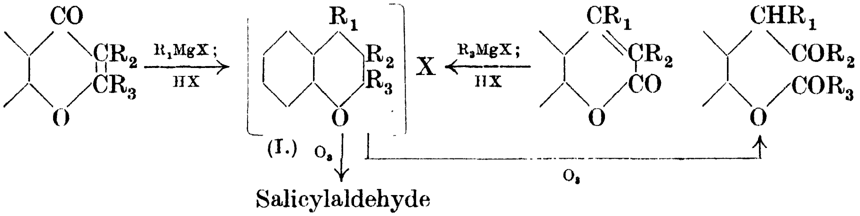
[64] J. L. Wood and L. F. Fieser, *ibid.*, 1941, **63**, 2323.

[65] G. M. Badger and J. W. Cook, *J.*, 1939, 802.

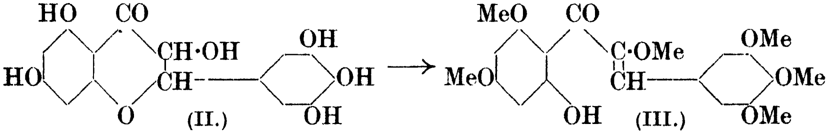
[1] S. Huzise and H. Tatsita, *Ber.*, 1941, **74**, 275.


COMe
O·COPh
CO
CH₂
COPh
OH
HBr
CO
Ph
O

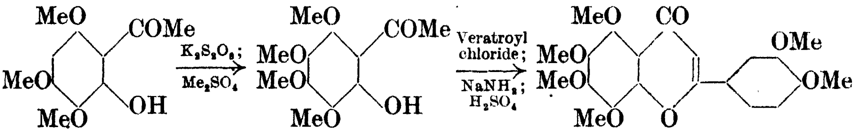
R. L. Shriner and R. B. Moffett[3] find that the same flavylium salt (I) results from the two syntheses shown, and in the ozonolysis of a related case have isolated products corresponding to both positions of the olefinic bond. They regard such substances as carbenium salts with the ionic charge on C_2 or C_4, and the independent existence of the two types as possible.


CO
CR₂
CR₃
O
R₁MgX;
HX
R₁
R₂
R₃
O
X
R₃MgX;
HX
CR₁
CR₂
CO
O
CHR₁
COR₂
COR₃
O
(I.)
O₃
O₃
Salicylaldehyde

Alpinetin, from *Alpinia chinensis*, has been identified as 5-hydroxy-7-methoxyflavanone.[4] The colouring matter of *Butea frondosa* is shown by methylation and hydrolysis to be the 3′-7-diglucoside of the flavanone butin, unusual in having a sugar residue in the unfused benzene ring.[5] *Ampelopsis meliæfolia* affords ampelopsin (II), one of the few natural flavanolones; its derivatives can be dehydrogenated to those of myricetin; and alkali converts hexamethylampelopsin into the chalkone (III), identified by synthesis.[6]


HO
CO
HO
CH·OH
CH
O
(II.)
OH
OH
OH
MeO
CO
MeO
C·OMe
CH
OH
(III.)
OMe
OMe
OMe

The simple 5-hydroxyflavone occurs in the primrose;[7] and Z. Horii[8] has synthesised nobiletin (IV), a pentahydroxybenzene derivative :


MeO
COMe
MeO
MeO
OH
K₂S₂O₈;
Me₂SO₄
MeO
COMe
MeO
MeO
MeO
OH
Veratroyl chloride;
NaNH₂;
H₂SO₄
MeO
CO
MeO
MeO
MeO
O
OMe
OMe

(IV.)

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[2] V. V. Ullal, R. C. Shah, and T. S. Wheeler, *J.*, 1940, 1499.

[3] *J. Amer. Chem. Soc.*, 1940, **62**, 2711; 1941, **63**, 1694.

[4] Y. Kimura, *J. Pharm Soc. Japan*, 1940, **60**, 87.

[5] P. S. Rao and T. R. Seshadri, *Proc. Indian Acad. Sci.*, 1941, *A*, **14**, 29.

[6] M. Kotake and T. Kubota, *Annalen*, 1940, **544**, 253.

[7] P. Karrer and G. Schwab, *Helv. Chim. Acta*, 1941, **24**, 297.

[8] *J. Pharm. Soc. Japan*, 1940, **60**, 246.

The *Linaria vulgaris* glycosides linarin and pectolinarin have been synthesised from the aglycones and acetobromorutinose; a third glycoside, *neo*linarin, is probably a crystalline form of the amorphous pectolinarin.[9]

The fruits of *Sophora japonica*[10] contain sophoricoside, identified by methylation and hydrolysis as genistein 4′-glucoside, and sophorabioside, formulated as genistein$\overset{4'\ 1}{\text{—}}$glucose$\overset{1}{\text{—}}$rhamnose. As well as these *iso*flavones there has been isolated sophoraflavonoloside, which appears to be campherol$\overset{3\ 1}{\text{—}}$glucose$\overset{2\ 1}{\text{—}}$glucose. Campherol also occurs, as its 7-diglucoside equisetrin, in *Equisetum arvense*.[11]

In *Persicaria hydropiper iso*rhamnetin is present as the potassium salt of its 3-sulphuric ester (persicarin).[12]

Hibiscus cannabinus flowers afford cannabiscitrin, a glucoside of the flavonol cannabiscetin, which, being oxidised to a quinone by *p*-benzoquinone, has hydroxyl groups in positions 5 and 8. Since the completely methylated glucoside yields on degradation 3 : 4-dimethylgallic acid, cannabiscitrin is 3 : 5 : 8 : 3′ : 4′-pentahydroxy-5′-glucosidoxyflavone, with the sugar group in the benzene moiety.[13] Quercetagetin occurs in *Tagetes erecta* as the monoglucoside quercetagitrin,[14] which does not behave as a 3-glucoside. Methylation and hydrolysis give pentamethylquercetagetin, which is oxidised to veratric acid but distinct from 5-hydroxy-3 : 6 : 7 : 3′ : 4′-pentamethoxyflavone, and in which the 7-position, *ortho* to the vacant position 8, for the free hydroxyl group is indicated by the smooth Claisen rearrangement of its allyl ether.

The furoflavone karanjin has been synthesised from karanjic acid *via* the methoxymethyl ketone.[15]

The fruits of the osage orange, *Maclura pomifera*, yield two pigments, osajin and pomiferin,[16] containing respectively two and three hydroxyl groups, one of which is methylated with difficulty. Tetrahydro-osajin dimethyl ether is readily converted by alkali into the ketone (V) with potassium formate, and then into homoanisic acid; it can also be degraded to (VI) together with anisic acid, while tetrahydropomiferin trimethyl ether by the same process gives (VI) with veratric acid. The pigments are thus *iso*flavones (VII) evidently with an attached terpene skeleton containing one ring and two double bonds; these are unconjugated, one linking an

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[9] G. Zemplén and R. Bognár, *Ber.*, 1941, **74**, 1818; G. Zemplén, R. Bognár, and L. Mester, *Ber.*, 1942, **75**, 489.

[10] G. Zemplén and R. Bognár, *ibid.*, p. 482; J. Rabaté and J. Dussy, *Compt. rend.*, 1936, **202**, 1117; 1937, **205**, 1431; J. Rabaté, *Bull. Soc. chim.*, 1940, **7**, 565.

[11] H. Nakamura and G. Hukuti, *J. Pharm. Soc. Japan*, 1940, **60**, 179.

[12] R. Kawaguchi and K. W. Kim, *ibid.*, 1937, **57**, 180; 1940, **60**, 174.

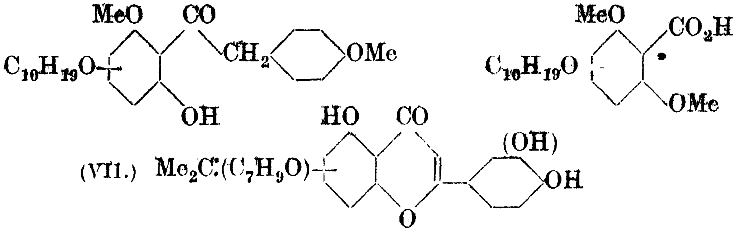
[13] P. S. Rao, T. R. Seshadri, and K. Neelakantam, *Proc. Indian Acad. Sci.*, 1941, *A*, **14**, 105; P. S. Rao and T. R. Seshadri, *ibid.*, p. 265.

[14] *Idem, ibid.*, p. 289.

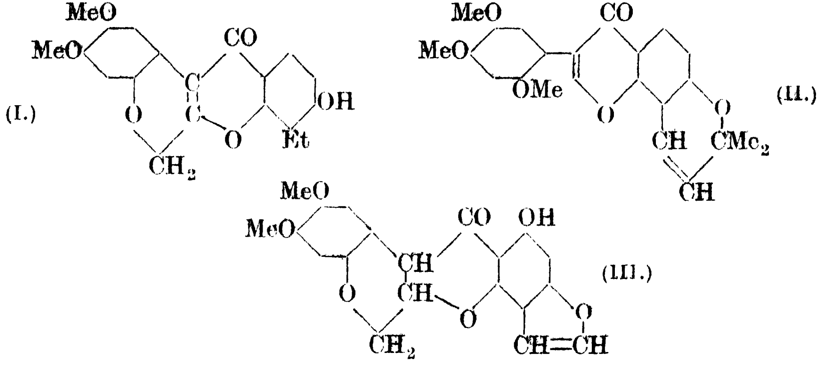
[15] T. R. Seshadri and V. Venkateswarlu, *ibid.*, 1941, *A*, **13**, 404; cf. *Ann. Reports*, 1939, **36**, 316.

[16] M. L. Wolfrom *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 574; 1939, **61**, 2832; 1940, **62**, 651, 1484; 1941, **63**, 422, 1248, 1253, 3356; 1942, **64**, 308, 311.

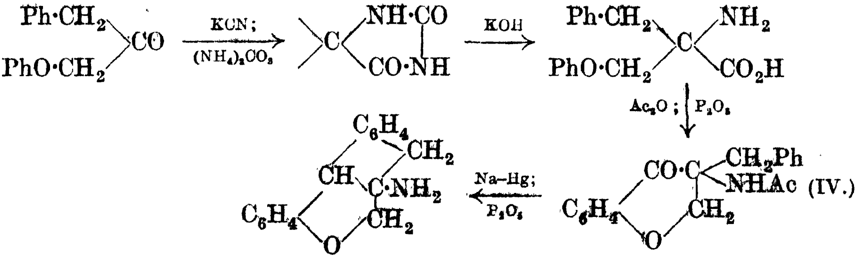
*iso*propylidene group, and one so placed as to interact with a hydroxyl group under the influence of sulphuric acid.


(V.) (VI.) (VII.)

Polycyclic Chromans.—The reduction and other transformations of elliptone have been studied, and its constitution confirmed through the synthesis of dehydrotetrahydroelliptone (I) by the method previously used for dehydrotetrahydrosumatrol.[17] *Derris malaccensis* resin contains malaccol,[18, 19] and a new phenol, possibly (II), which yields formic acid on alkaline hydrolysis, and resembles in this respect and in its colour reactions *iso*flavones synthesised from derritol methyl ether and related deoxybenzoins.[19, 20] Malaccol closely resembles sumatrol, and is believed to be 15-hydroxyelliptone (III).


(I.) (II.) (III.)

A new synthesis of the brazilin skeleton has been devised :[21]



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[17] S. H. Harper, *J.*, 1942, 587, 593; cf. T. S. Kenny, A. Robertson, and S. W. George, *J.*, 1939, 1601.

[18] T. M. Meijer and D. R. Koolhaas, *Rec. Trav. chim.*, 1939, 58, 207.

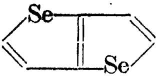
[19] S. H. Harper, *J.*, 1940, 309, 1178.

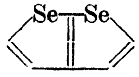
[20] *Idem*, *J.*, 1942, 595.

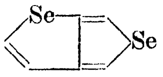
[21] P. Pfeiffer and H. Epler, *Annalen*, 1940, **545**, 263; P. Pfeiffer and H. Simons, *J. pr. Chem.*, 1942, **160**, 83.

The acid (IV, CO_2H for Ph), prepared similarly, was converted by nitrous acid into the corresponding hydroxy-compound, *dl*-brazilic acid, with racemisation if the optically active amino-acid were used.[22]

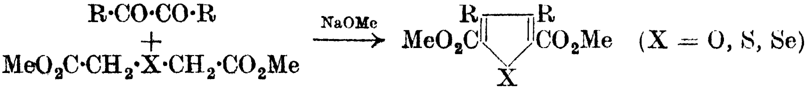
Thiophen Series.—W. Steinkopf and M. Boëtius[23] have prepared tetradeuterothiophen from tetrakischloromercurithiophen and deuterium chloride. The three possible selenophthens have been isolated from the products of interaction of acetylene and selenium, and oriented by determining their electric moments :[24]


$\mu = 0$


$\mu = 1{\cdot}52$ D.


$\mu = 1{\cdot}07$ D.

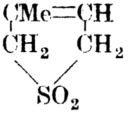
H. J. Backer and W. Stevens[25] have improved the Hinsberg synthesis of furans and thiophens and extended the method to selenophens :

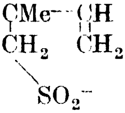


By heating 2-iodothiophen with copper, and by other related methods, a series of α-polythienyls was obtained, which were shown to be less saturated than the polyphenyls or polypyridyls by their increasing visual colour from terthienyl upwards and by their halochromy in sulphuric acid.[26]

The results of a detailed *X*-ray analysis of β-isoprene sulphone are not reconcilable with the accepted formula (I), and resonance with structures such as (II) is invoked to account for the equality in length of the C–C bonds in the ring.[27]

(I.)





(II.)

Nitrogen Ring Compounds.

Pyrrole Group.—Infra-red and Raman spectra are recorded for deuteropyrroles, effectively prepared as follows :[28]

$$C_4H_4NH \xrightarrow[\text{neutral}]{D_2O} C_4H_4ND \xrightarrow[\text{acid}]{D_2O} C_4D_4ND \xrightarrow[\text{neutral}]{H_2O} C_4D_4NH$$

Pyrrolidine is prepared by treating *N*-chloro-*N*-acyl-*n*-butylamines with sulphuric acid;[29] and formo-*o*-toluidide, with potassium *tert.*-butoxide at

---

[22] P. Pfeiffer and E. Heinrich, *J. pr. Chem.*, 1940, **156**, 261.

[23] *Annalen*, 1941, **546**, 208.

[24] B. Tamamushi, H. Akiyama, and S. Umezawa, *Bull. Chem. Soc. Japan*, 1939, **14**, 318; S. Umezawa, *ibid.*, p. 363.

[25] *Rec. Trav. chim.*, 1940, **59**, 423, 899.

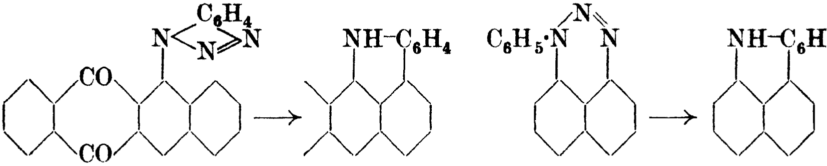
[26] W. Steinkopf, R. Leitsmann, and K. H. Hofmann, *Annalen*, 1941, **546**, 180.

[27] E. G. Cox and G. A. Jeffrey, *Trans. Faraday Soc.*, 1942, **38**, 241.

[28] F. A. Miller, *J. Amer. Chem. Soc.*, 1942, **64**, 1543; R. C. Lord and F. A. Miller, *J. Chem. Physics*, 1942, **10**, 328.

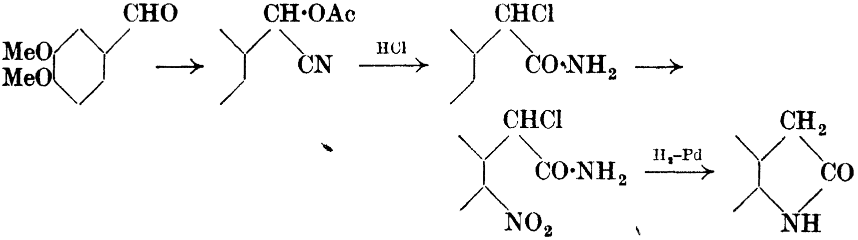
[29] G. H. Coleman, C. C. Schulze, and H. A. Hoppens, *Proc. Iowa Acad. Sci.*, 1940, **47**, 264; G. H. Coleman and G. Alliger, *ibid.*, 1941, **48**, 246.

350—360°, yields 46% of indole.[30] The carbazole synthesis by heating 1-arylbenztriazoles, now extended to nitro- [31] and aza- [32] derivatives, has also been effected across the *peri*-positions of naphthalene systems,[33] giving 4 : 5-benzacridans :



H. Adkins and H. L. Coonradt [34] find that nickel is an unsuitable catalyst for the selective reduction of a pyrrole ring attached to or fused with a benzene nucleus, unless that ring is made more sensitive by *N*-carbethoxylation. With copper chromite the heterocyclic ring only is attacked, except in the case of 2-phenylindole, which yields *cyclo*hexyl-indole and -indoline. By a method familiar in the pyrrole series, primary and secondary, but not tertiary, radicals are introduced into the 3-position of indole by the sodium alkoxide at 210—220°.[35] W. Borsche and H. Groth have acetylated many indoles in the 2- or 3-position with acetyl chloride or acetic anhydride, and a few 2 : 3-disubstituted indoles in the benzene nucleus by the Friedel–Crafts method.[36]

Oxindoles have been prepared in good yields by the reactions : [37]



Pyrolysis of 3-diazoacetyl-2-aminopyridine (from diazomethane and nicotinoyl chloride) affords 7-azaoxindole : [38] the related isatin and indigo are described.

Indophenines and Indigoid Colouring Matters.—G. Heller's formula (I) for indophenine is confirmed : isatin and α-thienylmagnesium bromide afford β-(α-thienyl)dioxindole, which can be dehydrated to indophenine; and the related pigments prepared from thiophen with benzil, or mesoxalic or benzoylformic esters, are degraded by alkali to derivatives of αα′-dithienyl.[39]

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[30] F. T. Tyson, *J. Amer. Chem. Soc.*, 1941, **63**, 2024.

[31] R. W. G. Preston, S. H. Tucker, and J. M. L. Cameron, *J.*, 1942, 500.

[32] E. Späth and K. Eiter, *Ber.*, 1940, **73**, 719; E. Koenigs and P.-L. Nantka, *Ber.*, 1941, **74**, 215.

[33] H. Waldmann and S. Back, *Annalen*, 1940, **545**, 52; H. Waldmann and K.-G. Hindenburg, *J. pr. Chem.*, 1940, **156**, 157.

[34] *J. Amer. Chem. Soc.*, 1941, **63**, 1563.

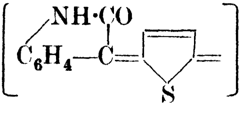
[35] (Mrs.) R. H. Cornforth and (Sir) R. Robinson, *J.*, 1942, 680.

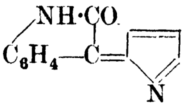
[36] *Annalen*, 1941, **549**, 238.

[37] G. Hahn and H. J. Schulz, *Ber.*, 1939, **72**, 1308; G. Hahn and M. R. Tulus, *Ber.*, 1941, **74**, 500.

[38] K. Miescher and H. Kägi, *Helv. Chim. Acta*, 1941, **24**, 1471; H. Kägi, *ibid.*, p. 141E.

(I.)

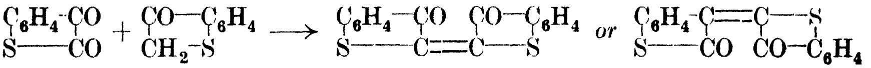




(II.)

P. Pratesi,[40] finding that pyrrole derivatives give the indophenine reaction if the *N*- and one α-position are free, proposed the structure (II) for the pigments. W. Steinkopf and H. Wilhelm[41] have prepared several pyrrole-blues in the same way as indophenine, from pyrryldioxindoles, and assign to them an analogous constitution, supported by molecular weight determinations. The production of a pigment from 2 : 4-dimethyl-3-ethylpyrrole is explained by displacement of the 2-methyl group to the nitrogen atom.

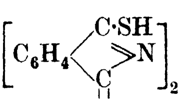
J. Harley-Mason and F. G. Mann[42] have studied the course of an extensive series of condensations of thionaphthenquinones with thioindoxyls :



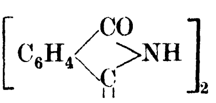
(III.) (IV.)

The results were curious : 4-substituted quinones always gave dyes of type (III); 7-derivatives gave different types with different thioindoxyls, but never mixtures; and all other quinones gave type (IV) products. Indoxyl, however, condensed with the β- and oxindole with the α-carbonyl group of all quinones.

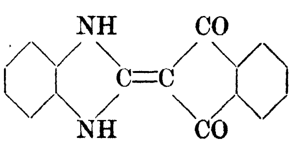
Phthalonitrile and its analogues are converted by ammonium sulphide into dithio-β-*iso*indigos (V), the reactions of which have been studied in detail. By hydrolysis of the *S*-dimethyl derivative, (V) yields β-*iso*indigo (VI), which is also obtained by heating monothiophthalimide with copper.[43]



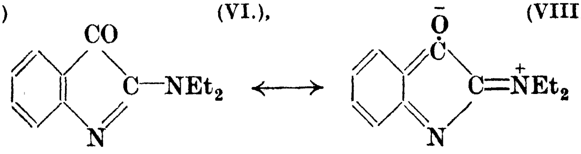
(V.)



(VI.),



(VIII.)



(VII.)

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[39] W. Steinkopf and W. Hanske, *Annalen*, 1939, **541**, 238.

[40] *Ibid.*, 1933, **504**, 258.

[41] *Ber.*, 1937, **70**, 2233; *Annalen*, 1941, **546**, 211.

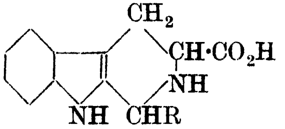
[42] *J.*, 1942, 404.

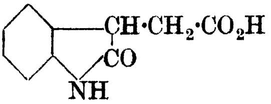
[43] H. D. K. Drew and D. B. Kelly, *J.*, 1941, 625, 630, 637; J. C. Porter, (Sir) R. Robinson, and M. Wyler, *ibid.*, p. 620.

J. van Alphen relates depth of colour in indogenides to extensive resonance with *o*-quinonoid structures, as in the violet base (VII). That participation of similar *o*-quinonoid structures is of importance for the colour of indigotin is suggested by the merely yellow colour of its isomeride (VIII), obtained by fusing 2-methylbenziminazole with phthalic anhydride.[44]

Tryptophan Derivatives.—The Adamkiewicz–Hopkins reaction depends on condensation with an aldehyde (glyoxylic acid), yielding a tetrahydrocarboline, which is oxidised to the colouring matter by impurities in the sulphuric acid; the test, in the absence of aldehyde, is diagnostic[45] for tetrahydrocarboline-γ-carboxylic acids (I, from tryptophan and R·CHO).

(I.)

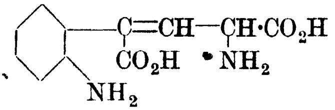


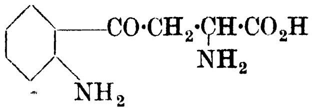


(II.)

One of the poisonous constituents of the fungus *Amanita phalloides* is the crystalline polypeptide phalloidine,[46] which contains no free amino- or hydroxyl groups and is formulated: 2 alanine + cysteine + 2 *l*-hydroxyproline (b) + hydroxytryptophan − $6H_2O$. The hydroxyproline is diastereoisomeric with the commonly occurring *l*-hydroxyproline (a). The structure (II) for hydroxytryptophan is supported by the development of a diazotisable amino-group on alkaline hydrolysis, and the negative Adamkiewicz–Hopkins and positive oxindole colour reactions.

(III.)





(IV.)

Kynurenine, an intermediate stage in the metabolic transformation of tryptophan into kynurenic (4-hydroxyquinoline-2-carboxylic) acid, has been regarded as (III), but A. Butenandt, W. Weidel, and W. von Derjugin now[47] conclude that it is a monobasic acid (IV) more obviously transformable into kynurenic acid, and have synthesised the racemic substance from ω-bromo-*o*-nitroacetophenone and ethyl phthalimidomalonate. Bacteria produce from tryptophan a compound of kynurenine and sucrose which can function as the v^+ hormone in *Drosophila*.[48] Tryptophan can be converted in the organism of the rat into another quinoline derivative, xanthurenic acid, recognized as 4 : 8-dihydroxyquinoline-2-carboxylic acid by synthesis from *o*-anisidine and ethyl oxaloacetate.[49]

[44] *Rec. Trav. chim.*, 1940, **59**, 289; 1941, **60**, 138.

[45] D. G. Harvey, E. J. Miller, and W. Robson, *J.*, 1941, 153.

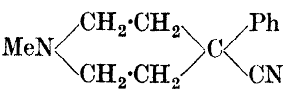
[46] F. Lynen and U. Wieland, *Annalen*, 1937, **533**, 93; H. Wieland and B. Witkop, *ibid.*, 1940, **543**, 171.

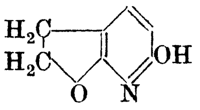
[47] *Naturwiss.*, 1942, **30**, 51; Y. Kotake and J. Iwao, *Z. physiol. Chem.*, 1931, **195**, 139.

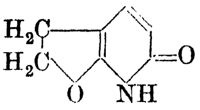
[48] E. L. Tatum and G. W. Beadle, *Science*, 1940, **91**, 458; E. L. Tatum and A. L. Haagen-Smit, *J. Biol. Chem.*, 1941, **140**, 575.

[49] L. Musajo and (Signa.) M. Minchilli, *Ber.*, 1941, **74**, 1839.

Six-membered Rings.—Di-(β-chloroethyl)methylamine condenses in presence of sodamide with phenylacetonitrile and other reactive methylene compounds—fluorene, *N*-methyloxindole, phenylmethylsulphone—yielding

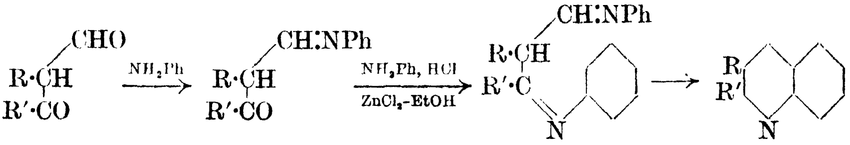

(I.)


(IIa.)


(IIb.)

piperidines (I); pyrans and thiopyrans have been made similarly.[50] Two stable, readily interconvertible substances are regarded as the hydroxypyridine (II*a*) and the pyridone (II*b*); only the former gives a coloration with ferric chloride.[51] The activity of the side chain in α-picoline and the like has been exploited in condensation with such reactive ketones as ethyl mesoxalate, alloxan, or benzil to give carbinols; [52] with cinnamaldehyde, yielding carbinols and then yellow phenylpyridylbutadienes; [53] and with formaldehyde and sulphanilamide to produce 2-(β-sulphanilamidoethyl)pyridine.[54]

2 : 3-Disubstituted quinolines (III) are effectively prepared by the interaction of arylamines and formyl (hydroxymethylene) ketones, the alternative



(III.)

3 : 4-compounds not being formed.[55] R. H. F. Manske, L. Marion, and F. Leger have prepared by unambiguous methods and fully characterised the seven mono- and 21 di-methylquinolines, as reference compounds for alkaloidal work.[56] The Friedel–Crafts reaction has limited application to quinolines and other condensed pyridines.[36] Hydrogenation of acridine takes the following course : [34]

$$\begin{tikzcd}
 & & {[C_{13}H_{17}N \text{ (symm.)} + C_{13}H_{17}N \text{ (unsymm.)} + C_{13}H_{21}N]} \arrow[d] \\
C_{13}H_9N \arrow[r, "\text{Ni or}", "CuCr_2O_4"'] & C_{13}H_{11}N \arrow[ur, "\text{Ni}"] \arrow[dr, "CuCr_2O_4"'] & C_{13}H_{23}N \\
 & & C_{13}H_{17}N \text{ (unsymm.)}
\end{tikzcd}$$

The water-soluble compounds of phosphorus oxychloride with acridone or its *N*-derivatives are formulated as (IV), because the Grignard reagent, which with the free oxychloride gives triphenylphosphine oxide, converts these compounds into diphenylphosphinic acids and diacridyl or diacriden (V), and because (IV, R = H) is hydrolysed to 5-chloroacridine.[57] Aniline,

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[50] O. Eisleb, *Ber.*, 1941, **74**, 1433.

[51] J. R. Stevens, R. H. Beutel, and E. Chamberlin, *J. Amer. Chem. Soc.*, 1942, **64**, 1093.

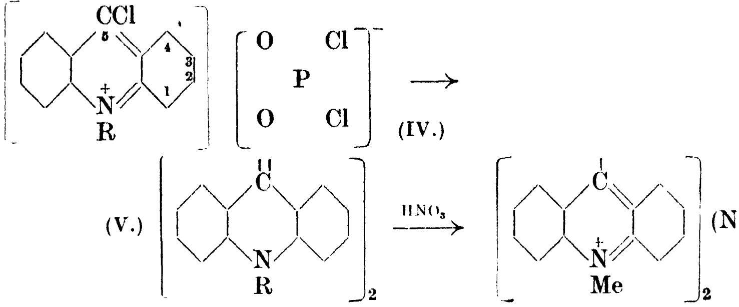
[52] S. M. McElvain and H. G. Johnson, *ibid.*, 1941, **63**, 2213.

[53] E. Späth, G. Kubiczek, and E. Dubensky, *Ber.*, 1941, **74**, 873.

[54] (Signa.) L. Monti and L. Felici, *Gazzetta*, 1940, **70**, 375.

[55] V. A. Petrow, *J.*, 1942, 693.

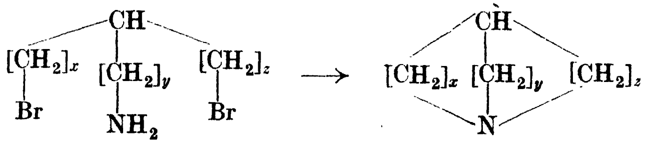
[56] *Canadian J. Res.*, 1942, **20**, *B*, 133.



(IV.) (V.) (VI.)

sodium hydrogen sulphide or thiosulphate, and potassium thioselenate, respectively convert the compounds (IV) into acridoneanils, thioacridones, and selenoacridones. Reduction with zinc dust readily affords the diacridens, which, except the 4 : 4′-disubstituted compounds, are strongly fluorescent and exhibit chemiluminescence in their atmospheric or peroxide oxidation. The diacridylium salts (VI = " lucigenin "), also obtained by reducing acridones with magnesium–magnesium iodide, fluoresce in neutral or acid solution, and are oxidised in alkaline media with most striking chemiluminescence, suppressed in this case also by 4 : 4′-substitution. The emission of light appears to be associated with the reduction of an intermediate peroxide; it is suggested that an earlier stage involves diradicals having the composition of diacridens, which are, however, diamagnetic. By heating with sulphur *NN′*-dimethyldiacriden is split into methylthioacridone; or, more readily, into methylacridone by successive action of thionyl chloride and water. Dixanthylene, diflavylene, and their thio-analogues, but not tetra-arylethylenes, undergo similar fissions.[58]

bicyclo-*Aza-alkanes*.[59]—Progress has been made with the synthesis of these ring systems, which occur in several groups of alkaloids. Compounds



(I.)

with a nitrogen atom as bridge-head (I) are advantageously prepared from dihalogeno-amines;[60] the substance (I; $y = 0, x = z = 5$), with fused seven-rings, has been so obtained, and 2- and 3-alkylquinuclidines have been produced as follows (R = tetrahydropyranyl) :

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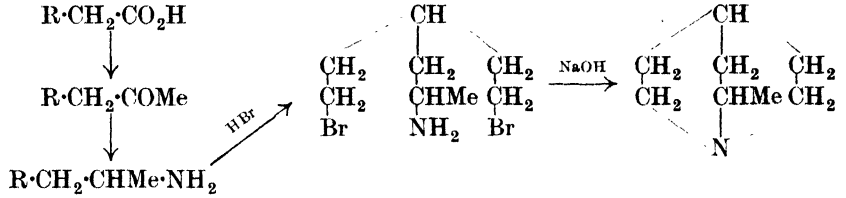
[57] K. Gleu and S. Nitzsche, *J. pr. Chem.*, 1939, **153**, 225, 233; K. Gleu, S. Nitzsche, and A. Schubert, *Ber.*, 1939, **72**, 1093; K. Gleu and R. Schaarschmidt, *ibid.*, pp. 1246, 1404; 1940, **73**, 909; K. Gleu and A. Schubert, *ibid.*, p. 805; B. Tamamushi and H. Akiyama, *Trans. Faraday Soc.*, 1939, **35**, 491.

[58] A. Schönberg and (Miss) W. Asker, *J.*, 1942, 272, 725.

[59] *Ann. Reports*, 1939, **36**, 321.

[60] V. Prelog *et al.*, *Annalen*, 1940, **545**, 229, 231, 243, 247, 256.


R·CH₂·CO₂H
R·CH₂·COMe
R·CH₂·CHMe·NH₂
HBr
CH
CH₂ CH₂ CH₂
CH₂ CHMe CH₂
Br NH₂ Br
NaOH
CH
CH₂ CH₂ CH₂
CH₂ CHMe CH₂
N

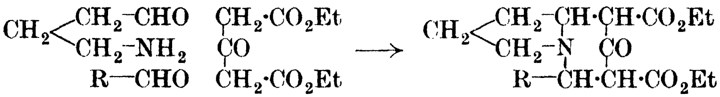
$$\left.\begin{array}{l}R\cdot COEt\\ CH_2Br\cdot CO_2Et\end{array}\right\} \longrightarrow R\cdot CEt{:}CH\cdot CO_2Et \longrightarrow R\cdot CHEt\cdot CH_2\cdot CO_2H \xrightarrow{HN_3}$$

$$R\cdot CHEt\cdot CH_2\cdot NH_2 \xrightarrow[NaOH]{HBr;} \text{3-ethylquinuclidine}$$

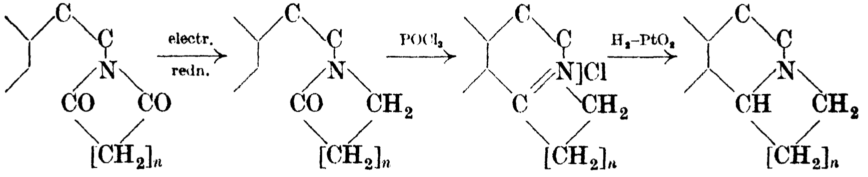
When heated with hydrobromic acid, ββ-diallylethylamine,

$$(C_3H_5)_2CH\cdot CH_2\cdot NH_2$$

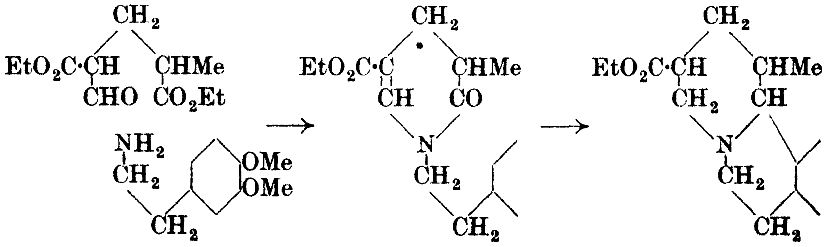
gave the dimethyl derivative of (I; $y = 1, x = z = 2$).[61] F. Lions and A. M. Willison[62] have effectively synthesised octahydropyrrocolines, by a variant of the Robinson tropinone synthesis, from ethyl acetonedicarboxylate, γ-aminobutaldehyde (as acetal), and a second aldehyde :


CH₂ CH₂–CHO
CH₂–NH₂
R—CHO
CH₂·CO₂Et
CO
CH₂·CO₂Et
CH₂ CH₂–CH·CH·CO₂Et
CH₂–N CO
R—CH·CH·CO₂Et

S. Sugasawa and co-workers[63] have prepared fused hydro*iso*quinoline systems by applying the Bischler synthesis to *N*-β-arylethyl derivatives of actams (n = 2, 3, 4) :


C
C
N
CO CO
[CH₂]ₙ
electr.
redn.
C
C
N
CO CH₂
[CH₂]ₙ
POCl₃
C
C
N]Cl
C CH₂
[CH₂]ₙ
H₂–PtO₂
C
C
N
CH CH₂
[CH₂]ₙ

In the same way they have prepared a benzpyridocoline derivative as a possible starting point for the synthesis of emetine :


CH₂
EtO₂C·CH CHMe
CHO CO₂Et
NH₂
CH₂
CH₂
OMe
OMe
CH₂
EtO₂C·C CHMe
CH CO
N
CH₂
CH₂
CH₂
EtO₂C·CH CHMe
CH₂ CH
N
CH₂
CH₂

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[61] R. Paul and H. Cottin, *Bull. Soc. chim.*, 1940, **7**, 626.

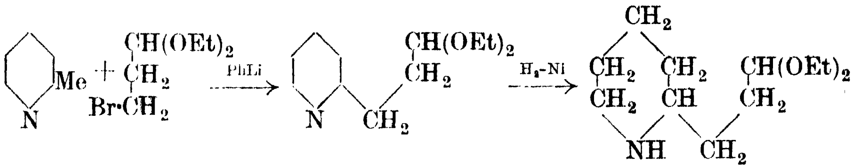
[62] *J. Proc. Roy. Soc. New South Wales*, 1940, **73**, 240.

[63] *J. Pharm. Soc. Japan*, 1937, **57**, 296; *Ber.*, 1938, **71**, 1860; 1939, **72**, 980; 1940, **73**, 782; 1941, **74**, 455, 459, 537; *Proc. Imp. Acad. Tokyo*, 1939, **15**, 82.

and derivatives of several of the possible dibenzpyridocolines, some of which could be dehydrogenated to quaternary compounds in which all four rings are aromatic.

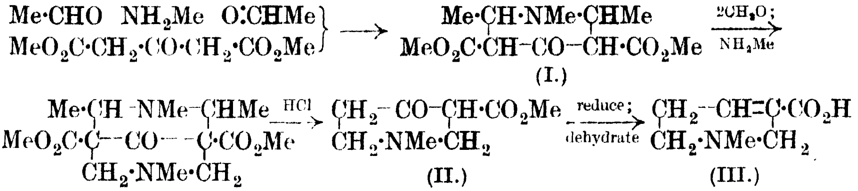
Alkaloids.

Simple Pyridine Bases.—Inactive pelletierine acetal has been synthesised[64] and converted into precisely identifiable derivatives of the unstable alkaloid :



The hydroxyl group in ψ-conhydrine is finally shown to be in position 5 by oxidation of dihydro-ψ-conhydrinemethine to *n*-hexyl dimethylaminomethyl ketone.[65]

P. S. Ugriumov[66] has synthesised arecaidine (III) by the route :

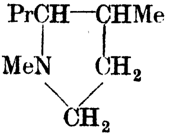


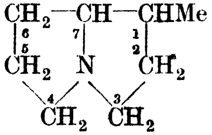
$$\left.\begin{array}{l}\mathrm{Me\cdot CHO\ \ NH_2Me\ \ O{:}CHMe}\\ \mathrm{MeO_2C\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2Me}\end{array}\right\}\longrightarrow\begin{array}{c}\mathrm{Me\cdot CH\cdot NMe\cdot CHMe}\\ \mathrm{MeO_2C\cdot CH{-}CO{-}CH\cdot CO_2Me}\\ \text{(I.)}\end{array}\xrightarrow[\mathrm{NH_2Me}]{\mathrm{2CH_2O;}}$$

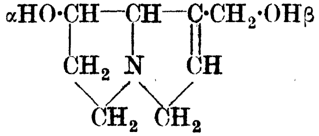
$$\begin{array}{c}\mathrm{Me\cdot CH{-}NMe{-}CHMe}\\ \mathrm{MeO_2C\cdot C{-}CO{-}C\cdot CO_2Me}\\ \mathrm{CH_2\cdot NMe\cdot CH_2}\end{array}\xrightarrow{\mathrm{HCl}}\begin{array}{c}\mathrm{CH_2{-}CO{-}CH\cdot CO_2Me}\\ \mathrm{CH_2\cdot NMe\cdot CH_2}\\ \text{(II.)}\end{array}\xrightarrow[\text{dehydrate}]{\text{reduce;}}\begin{array}{c}\mathrm{CH_2{-}CH{=}C\cdot CO_2H}\\ \mathrm{CH_2\cdot NMe\cdot CH_2}\\ \text{(III.)}\end{array}$$

and obtained stereoisomeric homologues by treating (I) in the same way as (II).

Senecio *Alkaloids.*[67]—*Senecio* and related species afford alkaloids which are esters of (usually) monoterpene acids of incompletely determined constitution, with amino-alcohols ("necines"), frequently retronecine. This mono-olefinic, dihydroxylic base has been converted into heliotridan under conditions unlikely to cause rearrangements; and the synthesis of *dl*-dihydroheliotridanmethine (I) completes G. P. Menschikov's[67] demonstration that heliotridan is 1-methylpyrrolizidine (II).[68] The isomeric 2-methylpyrrolizidine has also been synthesised.[69]


(I.)


(II.)


(III.)

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[64] M. A. Spielmann, S. Swadesh, and C. W. Mortenson, *J. Org. Chem.*, 1941, **6**, 780; J. P. Wibaut and M. G. J. Beets, *Rec. Trav. chim.*, 1940, **59**, 653.

[65] E. Späth and R. Lorenz, *Ber.*, 1941, **74**, 599.

[66] *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 48; *J. Gen. Chem. Russia*, 1941, **11**, 829.

[67] *Ann. Reports*, 1938, **35**, 328.

[68] R. Adams and E. F. Rogers, *J. Amer. Chem. Soc.*, 1941, **63**, 228.

[69] G. R. Clemo and T. A. Melrose, *J.*, 1942, 424.

Of the two hydroxyl groups in retronecine, one (β) is more readily esterified than the other (α); by hydrogenation, especially of the esters, the former group is usually replaced by hydrogen before the double bond is attacked; but free retronecine is reduced over nickel to a saturated dihydroxylic base inert to further hydrogenation, which is identical with platynecine, the basic moiety of platyphylline. These and other transformations are summarised :

$$\begin{tikzcd}
\begin{array}{c}\text{Retronecine}\\ \text{OH}\alpha,\ \text{OH}\beta,\ =\end{array} \arrow[r, "H_2\text{-}PtO_2", "\text{on ester}"'] \arrow[d, "H_2\text{-}Ni"'] & \begin{array}{c}\text{Deoxyretronecine}\\ \text{OH}\alpha,\ =\end{array} \arrow[r, "H_2\text{-}PtO_2"] & \begin{array}{c}\text{Retronecanol}\\ \text{OH}\alpha\end{array} \arrow[r] & \begin{array}{c}\text{ketone}\\ C_8H_{13}NO\end{array} \\
\begin{array}{c}\text{Platynecine}\\ \text{OH}\alpha,\ \text{OH}\beta\end{array} \arrow[r, "BzCl;", "SOCl_2"'] & \begin{array}{c}\text{chloro-ester}\\ \text{Cl}\alpha,\ \text{OBz}\beta\end{array} \arrow[r, "H_2\text{-}Ni;", "\text{hydrol.}"'] & \begin{array}{c}\textit{iso}\text{Retronecanol}\\ \text{OH}\beta\end{array} \arrow[r] & \begin{array}{c}\text{acid}\\ C_7H_{12}N{\cdot}CO_2H\end{array}
\end{tikzcd}$$

The β-hydroxyl group is thus primary and in the side chain, *C*-methyl determinations in this series being positive only in its absence, and its ready hydrogenolysis shows that the double bond is in the 1 : 2 or 1: 7-position. That retronecine is not a vinylamine derivative follows from its stability to acid and alkali, and from the observed increase in basic strength of retronecine and deoxyretronecine on hydrogenation, in contrast to the behaviour of authentic tertiary cyclic vinylamines. These results establish the formula (III) for retronecine, apart from the position of OHα, which is chosen to accommodate the formation of a cyclic ether stable to acid when retronecanol is treated with cyanogen bromide and then with alkali.[70]

Further *Senecio* species have furnished among others the following new bases : integerrimine,[71] longilobine,[71] and pterophine,[72] each of which is the ester of retronecine with a specific acid ; rosmarinine,[72] saponified to rosmarinecine and senecic acid ; otosenine,[73] which gives, probably, jaconecine, with a *mono*cyclic base ; and isatidine,[72] which is doubly abnormal in yielding monocyclic isatinecine with, apparently, a per-acid. The related species *Erechtites hieracifolia* and *Crotalaria Grantiana* afford hieracifoline[71] and grantianine,[74] esters of retronecine.

iso*Quinoline Alkaloids.*—Hunnemanine (I), from *Hunnemannia fumariæfolia*, is the first phenolic alkaloid of the ten-membered ring series. Its constitution follows from its methylation to *allo*cryptopine and the degradation of its ethyl ether to a known methoxyethoxy-*o*-toluic acid.[75] *Corydalis ophiocarpa* offers a more striking novelty in the di*iso*quinoline derivative ophiocarpine (II), hydroxylated in the position corresponding to the potential hydroxyl group of the phthalide-*iso*quinoline bases.[76] Ophiocarpine has been converted into tetrahydroberberine, is not a pseudo-base, and gives on oxidation the lactam (III; RR′ = CH_2O_2, R″ = H).

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[70] R. Adams and E. F. Rogers, *J. Amer. Chem. Soc.*, 1941, **63**, 537; R. Adams and J. E. Mahan, *ibid.*, 1942, **64**, 2588; R. Adams, M. Carmack, and J. E. Mahan, *ibid.*, p. 2593; R. Adams and K. E. Hamlin, *ibid.*, p. 2597.

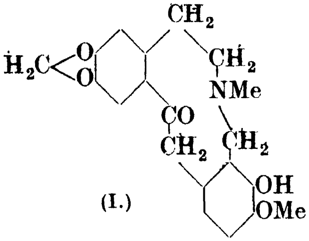
[71] R. H. F. Manske, *Canadian J. Res.*, 1939, **17**, *B*, 1, 8.

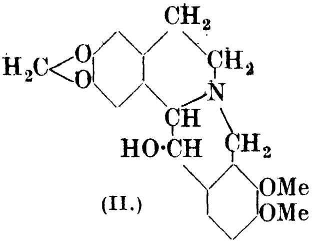
[72] H. L. de Waal, *Nature*, 1940, **146**, 777; *J. S. African Chem. Inst.*, 1941, **24**, 29; J. J. Blackie, *Pharm. J.*, 1937, **138**, 102.

[73] E. S. Schdanovitsch and G. P. Menschikov, *J. Gen. Chem. Russia*, 1941, **11**, 835.

[74] R. Adams, M. Carmack, and E. F. Rogers, *J. Amer. Chem. Soc.*, 1942, **64**, 571.

[75] R. H. F. Manske, L. Marion, and A. E. Ledingham, *ibid.*, p. 1659.


(I.)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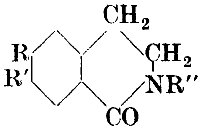
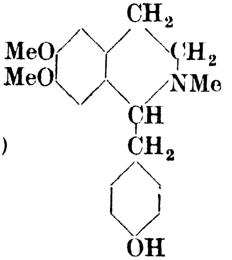
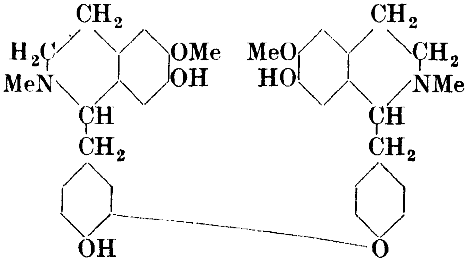
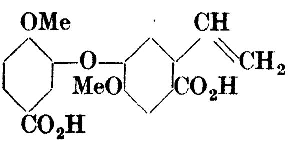

(III.)

Papaver armeniacum[77] yields armepavine, a methyl ether (IV) of coclaurine oxidisable to *p*-hydroxybenzoic acid and the lactam (III; R = R′ = OMe, R″ = Me). Dimerising dehydrogenation of coclaurine would lead to magnoline (V), isolated from *Magnolia fuscata*,[78] which gives by oxidation of its triethyl ether the lactam (III; R = OMe, R′ = OEt, R″ = Me) with 2-ethoxy-5 : 4′-dicarboxydiphenyl ether.


(IV.)


(V.)

The constitution assigned[79] to bebeerine (chondrodendrine), in which a pair of coclaurine structures are joined " head to tail " by *two* similar dehydrogenations, depended on its degradation to the acid (VI), which was decarboxyl-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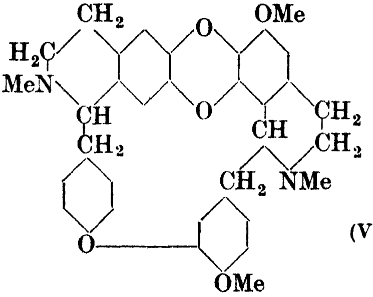
(VII.)

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[76] R. H. F. Manske, *Canadian J. Res.*, 1939, **17**, *B*, 51; 1942, **20**, *B*, 57.

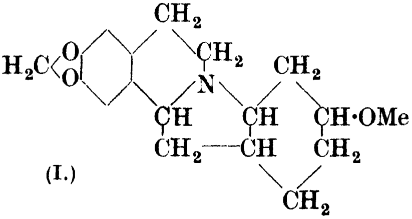
[77] S. Junusov, R. A. Konovalova, and A. P. Orékhov, *J. Gen. Chem. Russia*, 1940, **10**, 641.

[78] N. F. Proskurnina and A. P. Orékhov, *ibid.*, p. 707.

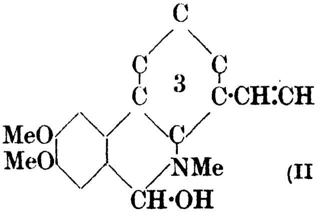
[79] *Ann. Reports*, 1937, **34**, 360.

ated and oxidised to a monobasic acid of established structure. The tribasic acid obtained by oxidation of (VI), and also of bebeerilene, the final product of Hofmann degradation of bebeerine, has now been unambiguously synthesised by F. Faltis, L. Holzinger, P. Ita, and R. Schwarz.[80] These authors emphasise the possible biogenesis of such alkaloids by successive dehydrogenations and methylations of coclaurine, and propose the modified formula (VII) for trilobine.

Erythrina *and* Lycoris *Alkaloids*.—Erythrina species afford, as well as hypaphorine (tryptophan methylbetaine), a series of "free" alkaloids,[81] isolated by the usual procedures and assigned names beginning with the element "erythr-," and also a series of "liberated" bases [82] extractable only after hydrolysis (? of water-soluble glycosides) and distinguished by the prefix "eryso-." Erythraline, $C_{16}H_{14}N(OMe)(O_2CH_2)$, is a tertiary base lacking NMe and CMe groups; it yields indole on potash fusion, oxidation of the methohydroxide affords 4 : 5-methylenedioxyphthalic acid, and the absorption spectrum of tetrahydroerythraline closely resembles that of 6 : 7-methylenedioxytetrahydro*iso*quinoline. It is suggested that tetrahydroerythraline, which is evidently tetracyclic with the nitrogen atom common to two rings, has the modified benzyl*iso*quinoline structure (I). Erythramine is dihydroerythraline, and erythratine a closely related base with an additional alcoholic hydroxyl group. The following "liberated" bases are phenolic, the first-named probably a catechol derivative : erysopine and erysonine, $C_{16}H_{16}O_2N(OMe)$; erysodine and erysovine, $C_{16}H_{15}ON(OMe)_2$.



(I.)



(II.)

Lycorenine, $C_{15}H_{12}(OH)_2(OMe)_2(NMe)$, yields a monoxime, and gives formaldehyde on ozonolysis, as does the nitrogen-free product of its Hofmann degradation. The latter also affords 3 : 4-dimethoxy-6 : 3′-dialdehydodiphenyl, the related acid having been synthesised.[83] Lycorenine is regarded as (II), with a hydroxyl group and a double bond in ring 3. Oxidation by lead tetra-acetate shows that the hydroxyl groups in dihydrolycorinone, and therefore in lycorine, are attached to adjacent carbon atoms.[84]

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[80] *Ber.*, 1941, **74**, 79.

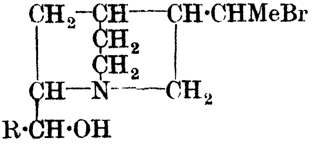
[81] K. Folkers and R. T. Major, *J. Amer. Chem. Soc.*, 1937, **59**, 1580; K. Folkers and F. Koniuszy, *ibid.*, 1939, **61**, 1232, 3053; 1940, **62**, 436, 1673; K. Folkers, F. Koniuszy, and J. Shavel, *ibid.*, 1942, **64**, 2146.

[82] *Idem, ibid.*, 1941, **63**, 1544; K. Folkers and F. Koniuszy, *ibid.*, 1940, **62**, 1677; K. Folkers and J. Shavel, *ibid.*, 1942, **64**, 1892; R. A. Gentile and R. Labriola, *J. Org. Chem.*, 1942, **7**, 136.

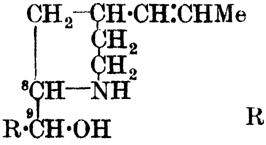
[83] H. Konda and T. Ikeda, *Ber.*, 1940, **73**, 867.

[84] H. Kondo and K. Katsura, *ibid.*, p. 112.

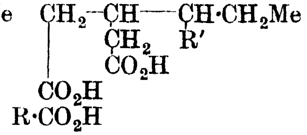
Cinchona Alkaloids.—Removal of halogen acid from halogenodihydroquinidine (I) gave a secondary base, niquidine, now separated into two components. These are regarded as geometrical isomerides (II),[85] since formaldehyde is formed in the reaction, and the niquidines afford on oxidation acetaldehyde and on reduction the same dihydroniquidine, oxidised by hydrogen peroxide to β-propylglutaric (III, R′ = H) and quininic acids. The same reagent oxidises dihydroquinidine to the acid (III, R′ = CO_2H).



(I.)



(II.)



(III.)

Niquine, derived from quinine, undergoes degradations analogous to those of the niquidines; and dihydroniquine, when boiled with acetic acid, yields dihydroniquidine and *epi*-C_9-dihydroniquidine by inversion at C_8 and C_9.[86]

The preparation of *epi*quinine and *epi*quinidine by epimerisation of quinine or quinidine has been improved,[87] and all four vinyl-free stereoisomerides synthesised.[88]

Aconite Alkaloids.—A secondary alcoholic group in mesaconitine and related bases has been oxidised to carbonyl, and the transformations of the ketones suggest that mesaconitine contains the structure

$$\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot \dot{C}(OMe)\cdot CH_2\cdot NMe\cdot.$$[89]

R. A. Konovalova and A. P. Orékhov,[90] among others, consider that the aconitines may be derived from a fundamental nucleus $C_{19}H_{28}NH$, and develop formulæ as follows :

Aconitine	$C_{19}H_{19}NEt(OH)_3(OMe)_4(OAc)(OBz)$
Mesaconitine	$C_{19}H_{19}NMe(OH)_3(OMe)_4(OAc)(OBz)$
Hypaconitine	$C_{19}H_{20}NMe(OH)_2(OMe)_4(OAc)(OBz)$
Pseudaconitine	$C_{19}H_{20}NEt(OH)_2(OMe)_4(OAc)(OVeratroyl)$
Indaconitine	$C_{19}H_{20}NEt(OH)_2(OMe)_4(OAc)(OBz)$
Bikhaconitine	$C_{19}H_{21}NEt(OH)(OMe)_4(OAc)(OBz)$
Lappaconitine	$C_{19}H_{22}NMe(OH)_2(OMe)_3(O\cdot CO\cdot C_6H_4\cdot NHAc)$

The much less toxic atisines are unesterified hydroxylic bases, of which the same authors have isolated four new examples from *Aconitum talassicum*;

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[85] E. M. Gibbs and T. A. Henry, *J.*, 1939, 240, 1294.

[86] W. Solomon, *J.*, 1941, 77.

[87] P. Rabe and H. Höter, *J. pr. Chem.*, 1939, **154**, 66.

[88] P. Rabe and G. Hagen, *Ber.*, 1941, **74**, 636; V. Prelog *et al.*, *ibid.*, p. 647.

[89] R. Majima and K. Tamura, *Annalen*, 1940, **545**, 1.

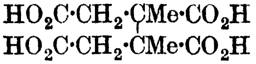
[90] *Bull. Soc. chim.*, 1940, **7**, 95; cf. W. Freudenberg, *Ber.*, 1936, **69**, 1962.

these last may be referred to the same nucleus as the aconitines if the *N*-substitutions (not yet investigated) are assumed to be as shown :

Talatisine	$C_{19}H_{23}NMe(OH)_3$	unsat.; dextrorotatory.
Talatisamine	$C_{19}H_{24}NH(OH)(OMe)_3$	inactive.
Talatisidine	$C_{19}H_{23}NEt(OH)_3(OMe)_2$	lævorotatory.
*iso*Talatisidine	,,	inactive.

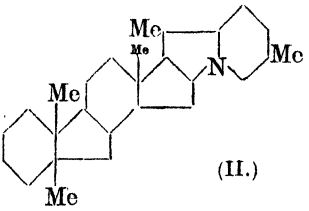
The original atisine from *A. heterophyllum*, now shown to be $C_{21}H_{30}NMe(OH)_2$ with two double bonds and at least one CMe group, gives 1-methylphenanthrene and another phenanthrene homologue $C_{17}H_{16}$ on dehydrogenation with selenium. The same plant affords the mono-olefinic hetisine, $C_{20}H_{27}O_3N$, and the saturated heteratisine, $C_{19}H_{25}NMe(OMe)(OH)_2(\cdot CO\cdot O\cdot)$, which may be related to the lactonic *Stemona* bases.[91] Napelline, $C_{21}H_{27}NMe(OH)_3$, which occurs with aconitine in *A. napellus*, yields on dehydrogenation phenanthrene homologues, including possibly the $C_{17}H_{16}$ hydrocarbon from atisine.[92] The tertiary base kobusine, $C_{20}H_{25}N(OH)_2$, occurs in *A. Sachalinense.*[93]

Sabadilla and Hellebore Alkaloids.—These fall into two classes : those, such as jervine, which are free hydroxylated bases not found in sabadilla seeds; and esters, like cevadine (tiglylcevine); it is suspected that the free and esterified alkamines are chemically related. Dehydrogenation of cevine [94] with selenium has afforded, as well as cevanthrol and cevanthridine (which may be $C_{25}H_{27}N$), 4 : 5-benzhydrindene, and β-picoline with its α′-ethyl and -hydroxyethyl derivatives. Other hydrocarbons separated chromatographically are regarded from their absorption spectra as derived from *cyclo*pentenofluorene. By oxidation cevine gave an acid $C_6H_{10}(CO_2H)_4$, which yielded a dianhydride and thence a keto-anhydride, and appeared to have two " primary " and two " tertiary " carboxyl groups, indicating unambiguously the formula (I). A further product was the lactone of a monocyclic acid $C_{10}H_{15}(OH)(CO_2H)_4$, convertible into decevinic acid, the structure proposed for which is now withdrawn. The skeleton (II) is suggested for cevine.

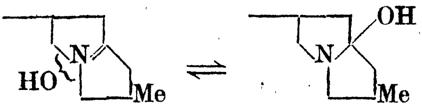


$$\begin{array}{l}HO_2C\cdot CH_2\cdot CMe\cdot CO_2H\\ \qquad\qquad\;\;|\\ HO_2C\cdot CH_2\cdot CMe\cdot CO_2H\end{array}$$

(I.)



(II.)



(III.)

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[91] A. Lawson and J. E. C. Topps, *J.*, 1937, 1640; W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, 1942, **143**, 589, 605.

[92] *Idem, ibid.*, p. 611; W. Freudenberg and E. F. Rogers, *J. Amer. Chem. Soc.*, 1937, **59**, 2572.

[93] H. Suginome and H. Simamouti, *Annalen*, 1940, **545**, 220.

[94] L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, 1941, **139**, 263, 293; **141**, 253; *idem*, with G. I. Lavin, *ibid.*, **139**, 277; cf. *Ann. Reports*, 1940, **37**, 379.

By dehydrogenation, protoveratrine gave several of the products obtained from cevine.[95] Jervine,[96] which is accompanied in white hellebore by the new mono-olefinic base veratramine, $C_{26}H_{33}O(NH)(OH)$,[97] gave on dehydrogenation 3-methyl-6-ethylpyridine with (probably) its 5-hydroxy-derivative, and hydrocarbons regarded on spectroscopic grounds as homologues of 4 : 5-benzhydrindene and 2 : 3-benzfluorene, but no base corresponding to cevanthridine.

Solanum *Alkaloids*.—Purapurine,[98] from *S. aviculare*, is identical with solasonine, which is [99] formulated: rhamnose — galactose — glucose — solasodine. Further reactions confirm the view that solasodine is a steroid derivative unsaturated at $C_5 - C_6$ and hydroxylated at C_3, and the behaviour on alkylation, hydrogenation, and bromination suggests a pseudo-basic system (III). *S. auriculatum* affords, with solasonine, the very similar solauricine, hydrolysed to rhamnose, galactose, glucose, and solauricidine.[1]

Erythrophleum *Alkaloids*.—The constituents of *E. Guineense*[2] are variable, some samples containing only erythrophleine and others only cassaine and its allies. These bases, with coumingine and coumingidine from *E. Couminga*,[3] are alkamine esters (see table) of diterpenoid acids derived from the tricyclic cassanic acid $C_{20}H_{34}O_2$, which yields 1 : 7 : 8-trimethylphenanthrene on dehydrogenation; cassaic acid is a ketodihydroxycassanic acid, and erythrophleic acid may be a methoxycassaic acid.

Erythrophleine ⟶ Erythrophleic acid + $NHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$
Cassaine ⟶ Cassaic acid + $NMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$
*Cassaidine ⟶ Dihydroxycassenic acid + $NMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$
Coumingine ⟶ Cassaic acid + $HO{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$ + $NMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$
Coumingidine ⟶ Cassaic acid (*inter alia*) + $NHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$

T. S. S.

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[95] L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, 1942, **143**, 427.

[96] W. A. Jacobs, L. C. Craig, and G. I. Lavin, *ibid.*, 1941, **141**, 51.

[97] K. Saito, *Bull. Chem. Soc. Japan*, 1940, **15**, 22.

[98] R. C. Bell and L. H. Briggs, *J.*, 1942, 1.

[99] L. H. Briggs, R. P. Newbold, and H. E. Stace, *J.*, 1942, 3; cf. *Ann. Reports*, 1940, **37**, 378.

[1] L. H. Briggs, J. J. Carroll, and R. C. Bell, *J.*, 1942, 12; L. H. Briggs and J. J. Carroll, *J.*, 1942, 17.

[2] F. Faltis and L. Holzinger, *Ber.*, 1939, **72**, 1443; B. K. Blount, H. T. Openshaw, and A. R. Todd, *J.*, 1940, 286; G. Dalma, *Helv. Chim. Acta*, 1939, **22**, 1497; L. Ruzicka and G. Dalma, *ibid.*, p. 1516; 1940, **23**, 753.

[3] L. Ruzicka, G. Dalma, and W. E. Scott, *ibid.*, 1941, **24**, 63, 179E; *idem* and B. G. Engel, *ibid.*, p. 1449; E. Schlittler, *ibid.*, p. 319E.

* Identical with "norcassaidine."

BIOCHEMISTRY.

1. NUTRITION.

FOR many years past it has been the habit of successive authors of the section on Biochemistry to begin the review of the year's work with a systematic account of the continual growth of knowledge about vitamins. We are breaking with tradition by skipping the theme on this occasion—notwithstanding its undiminished interest and importance—and devoting attention to two topics which seem ripe for review. The first is of particular interest during the war, namely, the evolution of new methods for the dehydration of foodstuffs by which their nutritive value may be left largely unimpaired. This, incidentally and in spite of our opening remark, will necessarily bring into the picture one aspect of applied vitamin chemistry. The second topic has to do with the other kind of " accessory food factors," as distinct from vitamins, namely, those inorganic " trace elements " essential for animal and plant health.

Dehydrated Foods.

A recent conference of The Nutrition Society was devoted to a description of the new developments in the preparation of dehydrated foods, and the original records may be consulted for the complete details.[1] The information released at this meeting is the fruit of several years' co-operative investigations carried out under the auspices of Government research departments. (Sir) E. Appleton,[2] Secretary of the Department of Scientific and Industrial Research, explained how the Low Temperature Research Station (Food Investigation Board) under F. Kidd at Cambridge had been mainly responsible for the experimental work on processing, and the Dunn Nutritional Laboratory (Medical Research Council) under L. J. Harris, also at Cambridge, for ensuring the preservation of nutritive values.

Dried milk and dried eggs have, it is true, long been familiar articles of commerce, and perhaps the most significant new departure, therefore, is that it is now possible for the first time to produce dried vegetables, which, after reconstitution and cooking, are not inferior to cooked fresh vegetables in respect of their principal dietetic virtue, *i.e.*, antiscorbutic potency, as well as in their palatability and appearance. It may be recalled that dried vegetables were not unknown in the last war, but they were then ineffective in preventing outbreaks of scurvy among the troops and were unattractive in colour and taste. Another aspect, which scarcely needs stressing in wartime, is the immense saving in shipping space which is effected when foods are imported in the dried state. It has been calculated that over 3000 tons of water were imported annually in our food before the war.[2] With dried meat there is the additional saving of refrigeration space, not to mention the room occupied by the bones and the other inedible parts of the carcase. Moreover, the dried products are sometimes more simple to prepare and cook than are the fresh, and it is an added convenience, for example, for armies in the field, to have their rations available in a compact, ready-for-use and non-perishable form. In one respect the dehydrated foods may even be regarded as nutritionally superior to the fresh : in the preliminary processing of vegetables to which they are subjected prior to the operation of dehydration, an enzyme, ascorbic oxidase, is inactivated ; in untreated foods this enzyme is able under some conditions to destroy the vitamin.

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[1] *Proc. Nutrit. Soc.*, July 25th, 1942 (vol. 1, 1943, in press); for abridged report, see *Chem. and Ind.*, 1942, **61**, 342; *Lancet*, 1942, **2**, 192, 186; *Brit. Med. J.*, 1942, **2**, 254; *Food Manufacture*, 1942, **17**, 291.

[2] *Proc. Nutrit. Soc.*, *ibid.*

We may cite, as a typical example, the procedure which is adopted in the dehydration of cabbage,[3] for retaining its vitamin C and its culinary " quality "—these two properties frequently, but not invariably, go together. The cabbage, cut into wide strips, is scalded in water containing a trace of sulphite. This step is necessary in order to protect ascorbic acid from subsequent oxidation and to prevent deterioration in appearance. To reduce the destruction of ascorbic acid, this scalding is done in the minimum amount of water, and for the least time necessary to inactivate the enzyme. Also the same water is used repeatedly to prevent undue loss of ascorbic acid by diffusion. Conditions of humidity, temperature, reaction, etc., are important during dehydration as well as during subsequent storage. For instance, dried cabbage is packed in an inert gas, in air-tight tins and at low relative humidity to preserve the vitamin. Such cabbage was reconstituted and cooked and tested in the R.A.F. : it was judged more palatable than ordinary cooked cabbage and found to contain twice as much vitamin C.[4]

By processes differing in points of detail it has been possible to produce dried carrots containing their full complement of carotene ;[3] dried meats active in vitamin B_1, nicotinic acid and riboflavin and with protein of high biological value ;[5] and dried eggs with vitamins A and D and protein-value unimparied.[5] Work on the drying of lean fish is also promising.[6]

After the war, we can expect that the use of dehydrated foods will have important economic consequences. It will make a wider choice of high quality commodities available to all sections of the community, and gluts will be more readily dealt with.[7] The dried foods will be needed in post-war relief; and ultimately we may expect that their use will affect the whole machinery of world distribution, storage and consumption of foodstuffs.[8]

Trace Elements.

Another of the last year's conferences of The Nutrition Society was devoted to a consideration of " Trace Elements in Relation to Health." [9] A fairly comprehensive review on " The Significance of Trace Elements in

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[3] R. J. L. Allen, J. Barker, and L. W. Mapson, *Food Manufacture*, 1942, **17**, 291.

[4] T. F. Macrae, *ibid.*

[5] E. M. Cruickshank, J. G. Sharp, and E. C. Bate-Smith, *ibid.*

[6] G. A. Reay, *ibid.* [7] (Sir) J. Barcroft, *ibid.* [8] J. Hammond, *ibid.*

[9] *Proc. Nutrit. Soc.*, Oct. 17th, 1942 (vol. 1, 1943, in press); abridged report in *Chem. and Ind.*, 1942, **61**, 463.

Nutrition " is also available.[10] Our object here will be to attempt a brief summing-up of the present position.

Definitions.—In the view of H. H. Green,[9] we should use the term " trace element " to include all those mineral elements normally or occasionally present in living tissues in small traces, no matter whether they are essential to health, or toxic, or apparently inert. The term has, however, frequently been restricted to such of these elements as are known to be essential to life, or has been sometimes still further limited to those which are essential to *animal* life (*e.g.*, by E. J. Underwood [10]). It would probably be better to keep to the first-mentioned definition. Then we can subdivide the trace elements into three classes. The first are the *essential* trace elements, namely, those which are needed for the maintenance of health, and are the normal constituents of cells, such, for example, as Cu and Zn. As C. R. Harington [9] has pointed out, we can only feel fully secure in admitting a claimant to this category when its biological function has been clearly defined : Cu and Zn do fulfil this test. The second class is that of the *abnormal* or *toxic* trace elements which may appear in some soils, pastures or drinking water and so cause damage to plant or animal health, *e.g.*, Se and Mo. The third class is that of the trace elements consistently occurring in living matter but for which no function has yet been traced : some elements in this class may yet prove to need promotion to Class 1 or Class 2. Furthermore, some trace elements appear to be needed by plants and not by animals, and the reverse may be true of others.

Trace Elements for Plants and Animals.—For example, boron is essential for plants, but apparently not for animals. Tungsten is said to stimulate early but not late growth in plants, but is likewise not known to be needed by animals. On the other side of the picture, Zn, Cu and Mn appear to be of relatively greater importance to the animal than to the plant.[11]

Enumeration of Trace Elements.—For animals the following appear to be the essential trace elements (apart from Fe, which is needed in more than " traces," and I, whose functions had long previously been recognised) : Co, Cu, Mn, and Zn. Some of the deficiency diseases caused by the absence of essential trace elements (*e.g.*, Cu and Co) occur spontaneously in animals in certain areas, one at least has only been produced experimentally (Zn). Elements which commonly occur in the tissues of higher animals but for which no function has yet been clearly defined include Ni, F, Si, As, Al, Rb, Br, Ba. Toxic trace elements, occurring naturally in soils, pastures or drinking water, and responsible for spontaneous disease in man or animals are F, Mo, and Se. Among the trace elements which in some circumstances may be necessary for, or may stimulate, the growth of plants are included Cu, Zn, W, and Mn. Some of these essential trace elements, *e.g.*, Cu, become toxic to plants when present in concentrations relatively higher although still so small absolutely as to merit the term " trace " ; and the same is true for animals.[10, 11]

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[10] E. J. Underwood, *Nutrit. Abstr. Rev.*, 1940, **9**, 515.

[11] See review by H. H. Green, *Proc. Nutrit. Soc.*, 1942, *loc. cit.*

Physiological Function and Enzyme Systems.—The rôle of a trace element cannot be clearly understood until it has been identified as a constituent of a compound or system possessing some definite biochemical action. We now have knowledge in these terms of the biochemical significance of two trace elements, Cu and Zn.[12] Although Cu has long been known to be present in hæmocyanin, the respiratory pigment of crustacea, and in turacin, a pigment in birds' feathers, it is only recently that T. Mann and D. Keilin [13] have isolated it from mammalian tissues in the form of crystalline Cu-protein compounds, hæmocuprein and hepatocuprein, from red blood cells and from liver respectively. Cu has also been proved to be a constituent of various polyphenol oxidase systems, *e.g.*, the polyphenol oxidase of potatoes [14]—responsible for their darkening when cut—that of mushrooms,[15] and laccase.[16] Other enzymes[18] which appear to be Cu-protein compounds are ascorbic oxidase[17] and indophenol oxidase.[19] Not less important is the discovery that zinc forms a part of the enzyme carbonic anhydrase, which is concerned in the transport and excretion of carbon dioxide and in maintaining the acid-base equilibrium of the body.[12, 20]

Deficiency of Co *and* Cu *in Farm Animals.*—A disease occurring spontaneously among sheep and cattle in some parts of Western Australia, known as " enzootic marasmus," has been traced to deficiency of Co.[21] Stock can now be kept free from the disease by the administration of a fraction of a milligram daily of a cobalt salt.[22] Similarly in Southern Australia the " coast disease " of sheep has been proved to be due to a combined deficiency of cobalt and copper.[23, 24] Diseases of cattle or sheep likewise due to deficiency of Co are the " bush sickness " of New Zealand,[25] the " pine " of Scotland,[26] the " salt-sick " of Florida,[27] the " nakuruitis " of Kenya, and a corresponding condition in Western Canada.[28] Also, several workers have had indications that a deficiency of cobalt may be one of the factors which lower resistance to helminthic infestation in Great Britain.[29]

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[12] See D. Keilin and T. Mann, *Proc. Nutrit. Soc.*, 1942, and earlier literature there cited.

[13] *Proc. Roy. Soc.*, 1938, *B*, **126**, 303.

[14] F. Kubowitz, *Biochem. Z.*, 1937, **292**, 221; 1938, **296**, 32.

[15] F. Keilin and T. Mann, *Proc. Roy. Soc.*, 1938, *B*, **125**, 187.

[16] *Idem, Nature*, 1939, **143**, 333.

[17] E. Stotz, C. J. Harrer, and C. G. King, *J. Biol. Chem.*, 1937, **119**, proc. xcv.

[18] Purified catalase contains Fe, but not Cu as for a time supposed by K. Agner, *Biochem. J.*, 1938, **32**, 1702.

[19] D. Keilin and E. F. Hartree, *Proc. Roy. Soc.*, 1938, *B*. **125**, 171.

[20] D. Keilin and T. Mann, *Biochem. J.*, 1940, **34**, 1163.

[21] J. F. Filmer, *Austral. Vet. J.*, 1933, **9**, 163; E. J. Underwood and J. F. Filmer, *ibid.*, 1935, **11**, 84; J. F. Filmer and E. J. Underwood, *ibid.*, 1937, **13**, 57; E. J. Underwood and R. J. Harvey, *ibid.*, 1938, **14**, 183.

[22] J. F. Filmer and E. J. Underwood, *ibid.*, 1937, **13**, 57.

[23] E. W. Lines, *J. Counc. Sci. Indust. Res. Austral.*, 1935, **8**, 117; H. R. Marston, *ibid.*, p. 111; H. R. Marston and I. W. McDonald, *Commonwealth Austral. Counc. Sci. Indust. Res. Bull.*, 1938, No. 113, 72 and 79.

[24] For a fascinating account of " Cobalt and other trace elements in relation to disease in Australia," see review by Sir C. J. Martin, *Proc. Nutrit. Soc.*, 1942, *loc. cit.*

[25] R. E. R. Grimmett and F. B. Shorland, *N.Z. J. Agric.*, 1935, **50**, 367; H. O. Askew and J. K. Dixon, *N.Z. J. Technol.*, 1936, **18**, 73; E. M. Wall, *ibid.*, 1937, **18**, 642.

[26] H. H. Corner and A. M. Smith, *Biochem. J.*, 1938, **32**, 1800.

[27] W. M. Neal and C. F. Ahmann, *J. Dairy Sci.*, 1937, **20**, 741.

A deficiency of copper has been shown to be responsible for diseases in farm animals occurring spontaneously in various restricted areas, *e.g.*, for "Lecksucht" in cattle in Holland,[30] "enzootic ataxia" of newborn lambs in parts of Western Australia,[31] or "swayback" in newborn lambs in England.[32, 33] "Swayback" is characterised by a macrocytic hyperchromic anæmia. The pathology has been studied by J. R. M. Innes.[33] The disease is prevented by administering Cu to the pregnant ewe or by using Cu salts as a top dressing on the deficient pastures.[34]

Experimental Deficiency of Co *and* Cu.—Long prior to the discovery of the spontaneously occurring Co-deficiency disease of farm animals just described, G. Bertrand and his collaborators [35] had proved that the element could be detected in animals' organs; and tests on mice [36] seemed to indicate its probably essential nature. Further work on rats,[37] however, was inconclusive, and thus it was left to the veterinarians to settle the issue, as recorded above.

With copper it was the other way, since the element had already been proved to be necessary for hæmoglobin formation in the rat.[38] Its function apparently is in the conversion of absorbed Fe into hæmoglobin [39] and it aids rapid hæmatopoiesis.

Mn *as an Essential Trace Element.*—The presence of traces of Mn in animal and vetegable tissues was first proved by G. Bertrand and F. Medigreceanu.[40] In rats kept on a diet devoid of Mn, an experimental deficiency-disease is produced, characterised by abnormalities in reproduction.[41] Lately, the question of Mn deficiency has emerged as of practical as well as theoretical importance, since diseases occurring spontaneously in fowls, known as "perosis" (or "slipped tendon") and "chondrodystrophy," have been traced to a lack of the element. The former disorder involves a malformation and crippling of the birds' legs, and the latter a deformity in the embryos.[42]

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[28] J. E. Bowstead and J. P. Sackville, *Canadian J. Res.*, 1939, **17**, 15.

[29] W. L. Stewart; E. L. Taylor, *Proc. Nutrit. Soc.*, 1942, *loc. cit.*

[30] B. Sjollema, *Biochem. Z.*, 1933, 267, 151; E. Brouwer, A. M. Frens, P. Reitsma, and C. Kalisvaart, *Landbouwk. Onderz. Rijkslandbouwprœfstation, Hoorn,* 1938, No. 44 (4) C, 267.

[31] H. W. Bennetts and F. E. Chapman, *Austral. Vet. J.*, 1937, **13**, 138; L. B. Bull, H. R. Marston, D. Murnane, and E. W. L. Lines, *Commonwealth Austral. Counc. Sci. Indust. Res. Bull.*, 1938, No. 113, 23.

[32] G. Dunlop and H. E. Wells, *Vet. Rec.*, 1938, **50**, 1175; J. R. M. Innes, *Proc. Nutrit. Soc.*, 1942, *loc. cit.*; T. Dalling, *ibid.*

[33] *Rep. Inst. Animal Pathol., Cambridge,* 1934, **4**, 227.

[34] H. W. Bennetts and A. B. Beck, *Austral. Vet. J.*, 1939.

[35] G. Bertrand and M. Mâcheboeuf, *Compt. rend.*, 1925, **180**, 1380, 1993.

[36] G. Bertrand and H. Nakamura, *ibid.*, 1927, **185**, 321.

[37] F. J. Stare and C. A. Elvehjem, *J. Biol. Chem.*, 1933, **99**, 473.

[38] E. B. Hart, H. Steenbock, J. Waddell, and C. A. Elvehjem, *ibid.*, 1928, **77**, 797.

[39] See review by C. A. Elvehjem, *Physiol. Rev.*, 1935, **15**, 471.

[40] *Ann. Inst. Pasteur*, 1913, **27**, 1, 282.

[41] E. R. Orent and E. V. McCollum, *J. Biol. Chem.*, 1932, **98**, 101.

Experimental Deficiency of Zn.—No instance is known of deficiency disease due to absence of Zn occurring spontaneously in men or animals. Nevertheless, the experiments of G. Bertrand and B. Benzon [43] on mice gave some preliminary suggestion that it was probably an essential element, and this was eventually proved more definitely by W. R. Todd, C. A. Elvehjem, and E. B. Hart,[43a], in their tests on rats, although the only symptoms so far recorded are diminished growth and poor fur.

Toxic Trace Elements and Farm Animals.—Two examples of diseases which occur spontaneously in farm animals in England, as a result of the absorption of traces of toxic elements from the soil of the pasturage, may be cited, namely, those caused by fluorine and molybdenum. Molybdenosis is seen in sheep and cattle in Somerset and elsewhere and is characterised by diarrhœa (" scouring "). The severity of the disease goes parallel with the amount of Mo in the pastures. It can be produced experimentally by administration of Mo salts. Treatment is by medication with copper sulphate, by changes in the pasture grown on the affected soil, or by making the soil more acid.[44]

Fluorosis in farm animals [45] is sometimes an " industrial disease," since it is seen near brick works, glass works, aluminium factories, or superphosphate factories, the fluorine being discharged into the atmosphere by the factory smoke and settling on the land. The animals affected show lameness, enlargement of bones and cachexia. An account of industrial fluorosis in England is given by F. Blakemore.[46]

Fluorosis in Humans.[47, 48, 49, 50, 51]—In the human, on the other hand, fluorosis, although sometimes an " industrial " disease,[51] seems to be associated more often with the use of drinking water, particularly well water, containing an undue amount of fluorine (*viz.*, more than about one part per million). Its symptoms are mottling of the enamel of the teeth, and, in more severe cases, osteosclerosis of the bones, especially the spine. It is seen not only in India, and in parts of America, but also in some areas in England,[48, 49, 50] there being an apparent relation between the fluorine content of the rocks or soil and the incidence of the disease.[52]

Fluorosis and Dental Disease in Humans.—It is known that fluorine is a normal constituent of the teeth, and it has been stated that there may be more F in sound teeth than in carious teeth. It is not surprising to learn, therefore, that it has been maintained in America, and evidence from England seems to support the claim,[53] that teeth which have been mottled by fluorosis are less liable to decay than are unmottled teeth. If this is so, we have another instance of a trace element which can be both " essential " and " toxic "; this would explain what, at first sight, appears to be the paradox of one disease (fluorosis) preventing another (caries).

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[42] For literature, see review by Underwood, *loc. cit.*

[43] *Compt. rend.*, 1922, **175**, 289.

[43a] *Amer. J. Physiol.*, 1934, **107**, 146.

[44] W. S. Ferguson, *Proc. Nutrit. Soc.*, 1942, *loc. cit.*

[45] See review by A. W. Peirce, *Nutrit. Abstr. Rev.*, 1939, **9**, 253.

[46] *Proc. Nutrit. Soc.*, 1942, *loc. cit.*

[47] M. C. Smith, *Amer. J. Publ. Health*, 1935, **25**, 696.

[48] M. M. Murray, *Proc. Nutrit. Soc.*, 1942, *loc. cit.*

[49] D. C. Wilson, *ibid.*

[50] F. H. Kemp, *ibid.*

[51] H. A. Krebs, *ibid.*

[52] C. N. Bromehead, *ibid.*

L. J. H.

2. IMMUNOCHEMISTRY.

It is obviously impossible in the space available to review the whole of the great output of papers on this subject which has appeared since the last Report, for 1940. Accordingly a somewhat arbitrary selection has had to be made.

Antigens.

Bacterial.—An antigenic polysaccharide built up of equimolecular proportions of acetylated *d*-glucosamine and galactose (but containing neither uronic acid nor pentose) was obtained from virulent and avirulent *B. anthracis* by G. Ivanovics.[1]

Bact. dysenteriæ Shiga has been shown to contain a protein neurotoxin [2] and a polysaccharide–protein–phospholipin somatic antigen,[3] the former being produced by both " rough " and " smooth " strains and the latter by " smooth " strains only. S. M. Partridge and W. T. J. Morgan [4] have shown that the somatic antigen complex can be dissociated by treatment with formamide into the non-antigenic phospholipin and a polysaccharide–protein moiety which has the somatic antigen properties of the " smooth " organisms. Treatment with trypsin gives the feebly antigenic phospholipin–polysaccharide. The free polysaccharide behaves as a hapten, reacting with anti-sera but being non-antigenic. The protein–polysaccharide complex can be split, by solution in 90% aqueous phenol and dialysis, to give the polysaccharide hapten and the antigenic protein, which, however, no longer carries the specific somatic antigenic properties of the complex.[5] The complex can also be degraded by boiling with 1% acetic acid; an almost non-antigenic protein is then obtained, which can be further dissociated by solution in phenol, probably with loss of a prosthetic group. The polysaccharide and the protein can be recombined by solution in formamide and precipitation with alcohol. If the conjugated protein is used, an antigen with the properties of the somatic antigen of *Bact. dysenteriæ* is produced; the simple protein, however, gives rise to a non-antigenic complex, suggesting that the prosthetic group is essential for antigenicity.

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[53] M. M. Murray, ref. 48; but cf. J. D. King, *Proc. Nutrit. Soc.*, 1942.

[1] *Z. Immun.*, 1940, **97**, 402.

[2] A. Boivin and A. Delaunay, *Compt. rend. Soc. Biol.*, 1940, **133**, 376; R. Prigge and L. Kicksch, *Z. Hyg.*, 1941, **123**, 417; T. Wagner-Jauregg and E. Helmert, *Angew. Chem.*, 1942, **55**, 21.

[3] W. T. J. Morgan and S. M. Partridge, *Biochem. J.*, 1940, **34**, 169.

[4] *Brit. J. Exp. Path.*, 1940, **21**, 180.

[5] W. T. J. Morgan and S. M. Partridge, *Biochem. J.*, 1941, **35**, 1140.

A similar antigenic complex has been isolated from *Bact. typhosum*, O 901, by E. Soru and C. Combiesco [6] and by W. T. J. Morgan and S. M. Partridge [7] by extraction with diethylene glycol. The latter showed that it is dissociated by boiling with 1% acetic acid into an ether-soluble phospholipin, a water-soluble polysaccharide, and an insoluble protein. The purified polysaccharide, 1·2% of organic phosphorus, less than 0·1% of N, $[\alpha]_{5461}$ + 128°, gave a precipitin reaction with anti-O serum. It was non-toxic to mice and not antigenic. The purified protein, 11·5% N, 0·47% P, $[\alpha]_{5461}$ −55°, soluble in alkali, but insoluble in acid, has properties very near to those of the corresponding protein from *Bact. dysenteriæ* Shiga, having the same absorption spectrum and giving rise to antibodies which react with the Shiga protein. The proteins can replace one another in combination with the polysaccharide of either organism to give antigens whose specificity corresponds to that of the polysaccharide. A similar protein, 10·7% N, 1·1% P, $[\alpha]_{5461}$ −50°, was also isolated from *Bact. dysenteriæ* Flexner 88. J. W. Palmer and T. D. Gerlough [8] prepared an antigenic substance from *Bact. typhosum*, by extraction with 85% phenol, which conferred immunity to living organisms when injected into mice.

J. H. Orr and G. B. Reed [9] obtained antigens having the characters of a polysaccharide from *Cl. welchii* by precipitation with alcohol of an extract made by boiling the cultures with acetic acid. The substance gave precipitates with homologous antisera.

S. C. Wong and T. Tung [10] and S. C. Wong [11] obtained protein and polysaccharide fractions from the various types of *C. diphtheriæ* and showed that the protein fractions contain at least a labile type-specific protein and a heat-stable protein common to the species. The specific antigen was lost with loss of virulence of the organism. The polysaccharides were very poor antigens and did not give precipitation reactions with antisera, although they gave complement fixation. It is claimed by L. Hoyle [12] that three lipoid antigens can be obtained from the *gravis*, *mitis* and *intermedius* types of *C. diphtheriæ* and from *C. hofmannii* by extraction with alcohol. By cross absorption experiments he showed them to be (1) a specific antigen, h, present only in *C. hofmannii*, (2) a specific antigen, d, characteristic of *C. diphtheriæ mitis* but probably also present in small amounts in *gravis* and *intermedius* strains, and (3) a group antigen, G, present in large amounts in *C. diphtheriæ gravis* and *intermedius* and in *C. hofmannii* and in small amounts in *C. diphtheriæ mitis*. It seems possible that the antigens are not really lipoids but either proteins or polysaccharides extracted with the lipoid.

Leuconostoc mesenteroides antisera give precipitin reactions with the polysaccharide, dextran, derived from broth cultures of the organism.[13]

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[6] *Compt. rend. Soc. Biol.*, 1940, **133**, 498.

[7] *Brit. J. Exp. Path.*, 1940, **23**, 151.

[8] *Science*, 1940, **92**, 155.

[9] *J. Bact.*, 1940, **40**, 441.

[10] *Proc. Soc. Exp. Biol. Med.*, 1940, **43**, 749.

[11] *Ibid.*, 1940, **45**, 850.

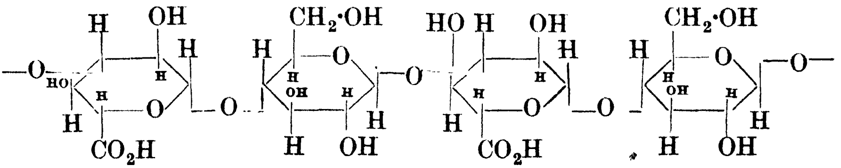
[12] *J. Hyg.*, 1942, **42**, 416.

[13] T. H. Evans, W. L. Hawkins, and H. Hibbert, *J. Exp. Med.*, 1941, **74**, 511.

E. J. Hehre [14] and E. J. Hehre and J. Y. Sugg [15] have shown that dextran can be synthesised from sucrose by an enzyme in sterile filtrates from *L. mesenteroides* and that the polysaccharide gives precipitin reactions with antisera to the homologous organism and to Types II, XII and XX pneumococci but not with antisera to Types I and III pneumococci. The polysaccharide is synthesised from no sugars other than sucrose and raffinose.

D. G. Evans [16] has shown that a heat-labile toxin can be obtained from *Hæmophilus pertussis* by freezing suspensions at low temperature and thawing, which will provoke antibodies in rabbits. The antisera neutralise the toxin *in vivo* and confer passive immunity when injected into animals. The toxin can be converted into a toxoid by the action of formaldehyde. Rabbits, actively immunised to *H. pertussis* toxin, are also protected against the toxins of *H. parapertussis* and *Brucella bronchiseptica*. *H. pertussis* antitoxin neutralises all three toxins equally. E. W. Flosdorf, A. Bondi, and T. F. Dozois [17] report that *H. pertussis* in Phase I contains heat-stable and heat-labile toxins, which are also present in the other phases of *H. pertussis* and in *H. parapertussis* but in much smaller amounts. Polysaccharide fractions have been isolated from *Br. bronchiseptica*, *H. pertussis* and *H. parapertussis* by extraction with hydrochloric acid or trichloroacetic acid or by tryptic digestion, followed by precipitation with alcohol;[18] that from *Br. bronchiseptica* is toxic to mice and rabbits, but the other two are not. They are antigenic and confer protection when injected into mice. Cross protection was found between the different strains.

R. E. Reeves and W. F. Goebel [19] have elucidated the structure of the soluble specific polysaccharide of Type III pneumococcus as being composed of glucose linked to C_3 of glucuronic acid and this by β-linkage to C_4 of a second glucose molecule :



Group specific proteins and type specific proteins and polysaccharides (the latter corresponding to those isolated by R. E. Hoffstadt and W. M. Clark [20] and by L. A. Julianelle and C. W. Wieghard [20a]) have been isolated by fractionation of the serological types of *Staphylococcus aureus* by W. F. Verwey.[21]

The group specific polysaccharide of hæmolytic streptococci has been shown by C. A. Zittle and T. N. Harris [22] to have 1·72% of nitrogen, 0·70% of phosphorus, and $[\alpha]_D$ $-71{\cdot}5^\circ$ and to give positive orcinol and glucosamine tests.

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[14] *Science*, 1941, **93**, 237.

[15] *J. Exp. Med.*, 1942, **75**, 339.

[16] *J. Path. Bact.*, 1940, **51**, 49; *Lancet*, 1942, **242**, 529.

[17] *J. Bact.*, 1942, **43**, 265.

[18] G. Eldering, *Amer. J. Hyg.*, 1942, **36**, 294.

[19] *J. Biol. Chem.*, 1941, **139**, 511.

[20] *J. Infect. Dis.*, 1935, **56**, 250.

[20a] *J. Exp. Med.*, 1935, **62**, 11, 31.

[21] *Ibid.*, 1940, **71**, 635.

[22] *J. Biol. Chem.*, 1942, **142**, 823.

The heat-labile, L, and heat-stable, S, antigens of vaccinia virus are probably carried by a single protein molecule, since both are associated with a single electrophoretically homogeneous component, and are precipitated in equal titre by antibodies to either of them. The active parts are differently affected by heat and by heat and alkali.[23] A nucleoprotein antigen has also been found in alkaline extracts of the elementary bodies of vaccinia.[24]

R. W. Linton [25] has given a good review of the chemistry and serology of the *Vibrio choleræ* group showing that the immunological grouping depends on the presence of specific protein and polysaccharide components. A. Damboviceanu and C. Barber [26] have described the "complete antigens" (O-antigens) of various types of *V. choleræ* and P. B. White [27] has continued his work on the antigenic fractions of S, R and ρ forms of the organisms.

A. J. Weil [28] has reviewed the work on the Wassermann antigen and related "alcohol-soluble" antigens. H. Brown and J. A. Kolmer, [29] from a study of the precipitate from "antigen" and syphilitic sera, came to the conclusion that the active substance is "an unknown, non-nitrogenous, phosphorus-containing substance" equally adsorbed on a mixture of lecithin and cephalin. J. Furth and E. A. Kabat [30] showed that the Wassermann hapten is associated with materials sedimented at high speed in the ultra-centrifuge. M. C. Pangborn [31] has isolated a phosphatide, cardiolipin, from ox heart, which, with lecithin and cholesterol, behaves as the Wassermann antigen. Cardiolipin contains 4·11% of phosphorus and 2·72% of sodium but no nitrogen, calcium, magnesium or sulphur. The ratio of Na to P is 1 : 1. On saponification it gives 62·2% of fatty acids and 30·4% of a water-soluble fraction which consists of non-reducing carbohydrate and has 13·4% of phosphorus. There is apparently no glycerophosphoric acid present.

Artificial Antigens.—Following their work on the somatic antigens of *Bact. dysenteriæ* Shiga and *Bact. typhosum,* Morgan and Partridge [32] coupled the conjugated protein fractions of these organisms with the non-antigenic polysaccharides agar, gum acacia and cherry gum by solution in formamide and precipitation with alcohol, and obtained antigens which provoked antibodies in rabbits having sharp specificity for the polysaccharides concerned. Gum acacia gave no precipitate with cherry gum antiserum, but cherry gum gave weak precipitation with gum acacia antiserum. Kanten, gum tragacanth, hyaluronic acid, the specific polysaccharides of Types I and II pneumococci and blood group A specific polysaccharide, isolated from mucin or peptone, gave no precipitates with the two gum antisera. Neither glucuronic nor galacturonic acid inhibited the reaction between gum acacia or cherry gum and the homologous antisera. W. T. J. Morgan[33] isolated a non-antigenic polysaccharide from commercial pepsin, peptone or gastric mucin, by extraction with 90% phenol and fractional precipitation, and showed that it could be coupled to the conjugated protein of *Bact. dysenteriæ* Shiga to give a powerful antigen, which on intravenous injection into rabbits gave rise to specific anti-" blood group A" agglutinins.

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[23] J. E. Smadel and T. M. Rivers, *J. Exp. Med.*, 1942, **75**, 151; T. Shedlovsky and J. E. Smadel, *ibid.*, p. 165.

[24] J. E. Smadel, T. M. Rivers, and C. L. Hoagland, *Arch. Path.*, 1942, **34**, 275.

[25] *Bact. Rev.*, 1940, **4**, 261.

[26] *Compt. rend. Soc. Biol.*, 1940, **133**, 501.

[27] *J. Path. Bact.*, 1940, **50**, 160, 165; **51**, 446, 447, 449.

[28] *Bact. Rev.*, 1941, **5**, 293.

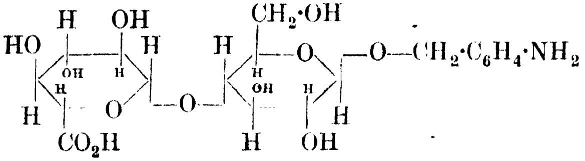
[29] *J. Biol. Chem.*, 1941, **137**, 525.

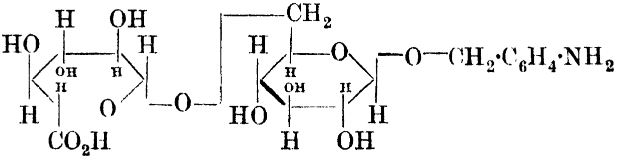
[30] *Science*, 1941, **94**, 46.

[31] *Proc. Soc. Exp. Biol. Med.*, 1941, **48**, 484; *J. Biol. Chem.*, 1942, **143**, 247.

[32] *Chem. and Ind.*, 1941, **60**, 722; *Brit. J. Exp. Path.*, 1942, **23**, 84.

W. F. Goebel[34] showed that artificial antigens containing hexuronic acids as determinant groups reacted with various antipneumococcal horse sera, but that their injection into animals conferred no protection against pneumococci. The injection of an antigen made by coupling synthetic diazotised *p*-aminobenzyl cellobiuronide (6-β-glucuronosidoglucose) with horse serum globulin, however, led to the production of antibodies which gave precipitates with Type III polysaccharide, agglutinated with Type III pneumococci, and conferred passive immunity on mice against virulent Types II, III and VIII pneumococci. The corresponding antigen containing gentiobiuronic acid (4-β-glucuronosidoglucose) gave rise to antisera which had no protective effect in mice against Types III and VIII pneumococci but conferred immunity against Type II organisms. Antigens containing cellobiose or gentiobiose instead of the corresponding aldobionic acids gave antibodies devoid of protective effect against pneumococci. Antigens containing the specific polysaccharides gave rise to antibodies with sharp type specificity, and antigens containing the unit pattern (aldobionic acid) yielded antibodies with a wider specificity covering all those types (*e.g.*, II, III and VIII) with specific polysaccharides built up from the same unit pattern.





Artificial antigens containing sulphonamides,[35] strychnine,[36] 1 : 2 : 5 : 6-dibenzanthracene and similar substances[37] and oxazolones[38] have been prepared. Hooker and Boyd[36] could not produce antibodies to an antigen containing morphine.

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[33] *Chem. and Ind.*, 1941, **60**, 722.

[34] *Nature*, 1939, **143**, 77; *Science*, 1940, **91**, 20; *J. Exp. Med.*, 1940, **72**, 33.

[35] A. G. Weddum, *Proc. Soc. Exp. Biol. Med.*, 1940, **45**, 218.

[36] S. B. Hooker and W. C. Boyd, *J. Immun.*, 1940, **38**, 479.

[37] H. J. Creech and R. N. Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 1661, 1670.

[38] W. Lettré, K. Bucholz, and M. E. Fernholz, *Z. physiol. Chem.*, 1941, **267**, 108.

It has been shown by F. C. Bawden and A. Kleczkowski[39] that such antigens as tomato bushy stunt virus, or human serum globulin, when heated with non-specific proteins, such as rabbit serum albumin, form complexes which retain their original specific antigenicity but are no longer able to precipitate with homologous antisera, behaving like haptens. Complement fixation occurs, showing that reaction between the complex and the antibody has taken place.

Since peptides with molecular weights between 600 and 1000 consisting of 8 to 12 amino-acid residues, obtained by the hydrolysis of silk, inhibit the precipitin reaction between silk fibroin and antibody, K. Landsteiner[40] infers that silk fibroin contains determinant groups not larger than such peptides and suggests that similar relations probably hold for other protein antigens.

D. Lackmann, S. Mudd, M. G. Sevag, J. Smolens, and M. Wiener[41] report that the specific precipitation between the nucleic acids of yeast, thymus and streptococci and certain antibacterial sera, particularly horse antipneumococcus antisera, is inhibited by purine nucleotides, purine nucleosides and purine bases, weakly inhibited by pyrimidine bases and not at all inhibited by pentoses and phosphate.

Antibodies.

Production.—An excellent monograph by F. M. Burnet[42] on the production of antibodies, reviewing the known facts and suggesting possibilities appeared during 1942. L. Pauling[43] in an extremely interesting paper suggests that all antibodies have the same polypeptide chains as normal serum globulins but differ from them in the configuration or folding of the chain, particularly at the ends. The modifications in configuration are introduced during the synthesis of the globulin from amino-acids in presence of the antigen, which impresses the effect of its determinant groups on the still mobile ends of the polypeptide globulin chain. Pauling suggests that the antibodies are bivalent in the sense that they have two reactive sites, one at each end of the chain, and that this is in conformity with the "lattice" hypothesis of antigen–antibody reactions. He adduces a considerable body of evidence in support of his theory, ranging from combining ratios to the effectiveness of antigens in provoking antibody production. As a result of this theory L. Pauling and D. H. Campbell[44] were led to the prediction that, if globulin were placed under mild denaturing conditions, such as heating at 50—60°, or solution in urea or alkali, and the condition then removed in the presence of an antigen, the polypeptide chains would unfold and then refold in a manner complementary to the antigen. By such treatment they succeeded in producing *in vitro* antibodies to 1 : 3-dihydroxybenzene-2 : 4 : 6-tri-*p*-azophenylarsonic acid, methyl-blue and the specific polysaccharide of Type III pneumococcus.

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[39] *Nature*, 1941, **149**, 593; *Brit. J. Exp. Path.*, 1941, **22**, 208; 1942, **23**, 169.

[40] *J. Exp. Med.*, 1942, **75**, 269.

[41] *J. Immun.*, 1941, **40**, 1.

[42] "The Production of Antibodies," Monographs from the Walter and Eliza Hall Institute of Research in Pathology and Medicine, No. 1. Macmillan and Co. Ltd., Melbourne, 1942.

[43] *J. Amer. Chem. Soc.*, 1940, **62**, 2643.

[44] *Science*, 1942, **95**, 440; *J. Exp. Med.*, 1942, **76**, 211.

P. R. Cannon [45] has pointed out that antibody production depends on the same factors as globulin synthesis and that a good response can only be expected if the amino-acid or protein intake of the animal is adequate. Lack of protein tends to lowered resistance to infection. R. Schoenheimer *et al.*,[46] by feeding amino-acids containing isotopic nitrogen to rats, have shown that serum globulin and antibodies are concerned in metabolic processes involving dietary nitrogen and that the half-life period of an antibody molecule is about two weeks. Antibodies introduced by passive immunisation do not undergo such changes, suggesting that antibodies are still being produced during active immunisation, even when the amount in circulation is diminishing, until an equilibrium is reached. Passively introduced antibody, on the other hand, disappears more rapidly and is not replaced by synthesis.

Purification.—Further work on the purification of antibodies by the action of proteolytic enzymes has been reported. F. Modern and G. Ruff [47] increased the purity of antitetanus serum from 7000 units per gram of protein in the original serum to 22,500 units per gram of protein by the consecutive action of pepsin and papain and precipitation with 22% sodium sulphate solution, but with a loss of about 50% of the antitoxin. A. L. Petermann and A. M. Pappenheimer [48] digested the euglobulin fractions of horse antisera to Types I and II pneumococci with pepsin and obtained antibody which was homogeneous in the ultra-centrifuge, with a molecular weight less than 100,000; the purified antibody combined with twice as much specific polysaccharide per mg. of nitrogen as did the original antibody, and was comparable with normal rabbit antipneumococcus antibody in size and combination with polysaccharide. M. L. Petermann [49] split horse diphtheria antitoxin, by the action of papain, into equal fragments (as determined by the ultra-centrifuge), only one of which flocculated with toxin; it was soluble in 5% sodium chloride solution at 58° and pH 4·2. These " half " molecules can be further broken down to " quarter " molecules. J. H. Northrop [50] obtained crystalline diphtheria antitoxin by the digestion of toxin-antitoxin floccules with trypsin at pH 3·7 and fractionation with ammonium sulphate. The product was homogeneous in the ultra-centrifuge and electrophoresis apparatus, had a molecular weight about 80,000, and contained 700,000 to 10^6 units per gram of nitrogen.

By dialysis of rabbit antipneumococcus sera S. Rafael, C. F. Pait, and

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[45] *J. Immun.*, 1942, **44**, 107.

[46] R. Schoenheimer, S. Ratner, D. Rittenberg, and M. Heidelberger, *J. Biol. Chem.*, 1942, **144**, 541, 545.

[47] *Compt. rend. Soc. Biol.*, 1940, **133**, 158.

[48] *Science*, 1941, **93**, 458.

[49] *J. Biol. Chem.*, 1942, **144**, 607.

[50] *Science*, 1941, **93**, 92.

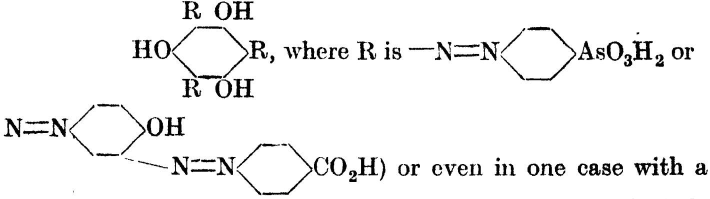
M. C. Terry[51] showed that the antibody is associated with pseudo- and eu-globulins in different proportions depending on the intensity of immunisation. The less avid antibody produced in the early stages of immunisation is associated with the euglobulin. With progressive immunisation the antibody becomes more avid and more of it is associated with the pseudoglobulin and less with the euglobulin. The ratio of pseudoglobulin to total globulin increases with prolonged immunisation. R. A. Kekwick and B. R. Record,[52] by electrophoretic analysis, also found that the distribution of diphtheria antitoxin between β- and γ-globulin altered with the progress of immunisation. The first response is the production of antibody associated with γ-globulin, which combines more rapidly with toxin but affords a somewhat unstable complex expressed by the formula TA_4. With further injections the amount of γ-globulin antitoxin remains about constant but β-globulin antitoxin is formed; this has a longer flocculating time and gives a more stable complex having the formula TA_2.

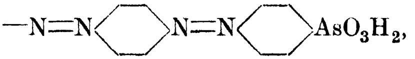
A. Kleczkowski[53] and F. C. Bawden and A. Kleczkowski[54] offer an explanation of the apparently greater heat stability of H-type antibodies as compared with O-antibodies. They state that the antibodies are equally susceptible to heat but that the antibodies to O-antigens form complexes with non-specific proteins (*e.g.*, albumin) more readily than do antibodies to H-antigens; the complexes combine with antigen, as shown by complement fixation experiments, but do not precipitate (compare the similar findings with heated protein antigens).[39]

Antigen–Antibody Reactions.

Interest in this field has mainly centred on the " valence " of antigens and antibodies and the development of theories describing quantitatively the reactions between antigens and antibodies.

S. B. Hooker and W. C. Boyd[55, 56] by using a number of haptens of known constitution, tested the prediction from the " lattice " or " alternation " hypothesis that bivalent haptens and the corresponding antibodies should form precipitates. They came to the conclusion that the " lattice " theory is probably not true, since precipitation did not occur even with tervalent haptens (that is, haptens containing three active groups; for example,



or even in one case with a sexavalent hapten, although combination between the hapten and antibody had occurred, since inhibition of subsequent precipitation with the homologous antigen was observed. It is suggested that, if the haptens carry many polar or " solubilising " groups, combination with the antibody is not adequate to render the complex insoluble. This is borne out by the fact that acetylation or benzoylation of such polar groups converts non-precipitable haptens into precipitable ones. From this basis Boyd [56] developed his " occlusion " theory of precipitin reactions, according to which precipitation depends on the reduction of the solubility of the complex below the point at which it can remain in solution by mutual neutralisation of the polar groups of the antibody and antigen or hapten and by the blocking off, or occlusion, of the polar groups of closely neighbouring antibody molecules. If the active groups of a hapten molecule are close together, there may not be room for two or more molecules of antibody (steric hindrance), so their polar groups cannot be occluded and precipitation does not occur (compare the example quoted above). If, however, the hapten molecule is larger, for example when R of the above formula is  the polar groups are further apart, more antibody molecules may be able to react, and a larger number of polar groups can be occluded with consequent precipitation. The decisive factors seem to be the number of polar groups of the antigen or hapten left free after combination with the antibody, and the distance separating the active groups, which determines the amount of steric hindrance exerted by one antibody molecule on another.

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[51] *J. Immun.*, 1940, **39**, 317, 337, 349.

[52] *Brit. J. Exp. Path.*, 1941, **22**, 29.

[53] *Ibid.*, p. 188.

[54] *Ibid.*, 1942, **23**, 178.

[55] *J. Immun.*, 1941, **42**, 419.

[56] W. C. Boyd, *J. Exp. Med.*, 1942, **75**, 407.

By immunising rabbits with arsenil-sheep globulin, containing the two determinant factors phenylarsonic acid and the species specific sheep protein, and fractional precipitation of the antisera, F. Haurowitz and P. Schwerin [57] concluded that the antibody molecules are mainly univalent, that is, each corresponds to one determinant group only. The antigen–antibody precipitate is considered to consist of aggregates of complex particles containing a multivalent antigen molecule to which are attached several univalent antibody molecules. S. B. Hooker and W. C. Boyd [58] review the evidence on the " valence " (in the sense of the number of active groups) of antigens and antibodies and conclude that antigenic proteins, having a molecular weight of about 35,000, seem to have a minimal functional valence of five with an upper limit less than thirty. Larger antigenic molecules probably have a higher valence, which is likely to be proportional to their surface area. Although the evidence in the case of antibodies is still inadequate, the bulk of it favours the view that they are univalent or, less probably, bivalent.

A. D. Hershey [59] has developed a quantitative theory of the antigen–antibody reaction based on the " lattice " theory and the assumption of multivalent antigen and antibody molecules. The dissociation of the complexes being taken into account, the quantitative relations o the composition of the precipitate, velocity of flocculation and optimal proportions are developed. The valence of antibody is considered to be not more than 2.

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[57] *Brit. J. Exp. Path.*, 1942, **23**, 146.

[58] *J. Immun.*, 1942, **45**, 127.

[59] *Ibid.*, 1941, **42**, 455, 485, 515; 1942, **45**, 39.

The solubility of antigen–antibody precipitates in excess of antigen is considered by W. C. Boyd,[60] who also demonstrated [61] that most antisera can be grouped into (*a*) an H type comprising horse sera and some rabbit sera, which give optima by both " constant antibody " and " constant antigen " flocculation procedures, and (*b*) an R type, to which most rabbit sera belong, which give optima only by the " constant antibody " method. The differences are accounted for by the chemical and physical properties of the antisera. The velocity of combination of the pneumococcus polysaccharides with antibody is dealt with by M. Mayer and M. Heidelberger,[62] and S. C. Liu and H. Wu [63] describe the acid and alkaline dissociation of such precipitates.

Very interesting demonstrations of the combination of antigen and antibody have been given by the use of the electron-microscope, for example, in the case of tobacco mosaic virus and its antiserum.[64]

Toxins.

A number of papers dealing with the purification and chemistry of toxins have appeared. A. M. Pappenheimer [65] has dealt with diphtheria toxin, which has the properties of a protein. W. McD. Hammon [66] found that staphylococcus enterotoxin behaved as a large complex carbohydrate molecule, and I. A. Parfentjew, F. L. Clapp, and A. Waldschmidt [67] showed that staphylococcus toxin can be toxoided, without loss of antigenicity or specificity, by peptic digestion at pH 4·6—5·2. Scarlatinal toxin has the properties of a protein of low molecular weight and is probably not conjugated, according to E. S. G. Barron, G. F. Dick, and C. M. Lyman.[68] W. L. Koerbner and W. E. Bunney,[69] on the other hand, claim to have isolated a protein-free toxin. G. A. Hottle and A. M. Pappenheimer [70] and A. H. Stock [71] and his co-workers [72] describe the toxin as a protein which is relatively resistant to pepsin, papain and trypsin and is heat-coagulable. The oxygen-labile hæmolysin, streptolysin-O, appears to be a protein whose activity depends on the presence of SH groups, which become reversibly converted into the dithio-group, S-S, upon inactivation of the toxin by oxygen, according to C. V. Smythe and T. N. Harris [73] and to E. W. Todd.[74] The latter worker [74,75] has shown that streptolysin-O is neutralised by antisera to *Cl. welchii* θ-toxin, which is also oxygen-labile, but not by antisera to the stable α-toxin. θ-Toxin is neutralised by high titre streptolysin-O antisera. All the known oxygen-labile hæmolysins which are reactivated on reduction

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[60] *J. Immun.*, 1940, **38**, 143.

[61] *J. Exp. Med.*, 1941, **74**, 369.

[62] *J. Biol. Chem.*, 1942, **143**, 567.

[63] *Proc. Soc. Exp. Biol. Med.*, 1940, **43**, 747.

[64] T. F. Anderson and W. M. Stanley, *J. Biol. Chem.*, 1941, **139**, 339.

[65] *J. Bact.*, 1942, **43**, 273.

[66] *Amer. J. Publ. Health*, 1941, **31**, 1191.

[67] *J. Immun.*, 1941, **40**, 189.

[68] *J. Biol. Chem.*, 1941, **137**, 267.

[69] *J. Immun.*, 1941, **40**, 459.

[70] *J. Exp. Med.*, 1941, **74**, 545.

[71] *J. Biol. Chem.*, 1942, **142**, 777.

[72] L. E. Krejci, A. H. Stock, E. B. Sanigar, and E. O. Kraemer, *ibid.*, p. 785.

[73] *J. Immun.*, 1940, **38**, 283.

[74] *Biochem. J.*, 1941, **35**, 1124.

[75] *Brit. J. Exp. Path.*, 1941, **22**, 172.

(from streptococci, pneumococci, *Cl. tetani* and *Cl. welchii*) are closely related serologically but are not identical. The hæmolysins of staphylococci, *Cl. septicum* and *Cl. œdematiens*, which are irreversibly destroyed by oxygen, are not neutralised by antitoxins to toxins of the first group.

The opalescence produced in normal human sera by the α-toxin of *Cl. welchii* (the Nagler phenomenon) was shown by R. G. Macfarlane, C. L. Oakley, and C. G. Anderson [76] to be due to the liberation of free fat and to require the presence of calcium ions. A similar but more rapid and more sensitive liberation of fat is produced by the action of α-toxin on lecitho-vitellin. The reaction can be used for the titration of α-toxin. It has been shown by M. G. Macfarlane and B. C. J. G. Knight [77] that the α-toxin acts as a lecithinase which causes splitting of lecithin to phosphorylcholine and a diglyceride. It is suggested that the lecithin acts as a stabiliser in the serum or lecitho-vitellin and that the fat can aggregate when the lecithin is destroyed. E. M. Crook [78] showed that the Nagler reaction was given by fowl serum but not by horse, pig, sheep or rabbit sera. *Cl. septicum*, *Cl. histolyticum*, *Cl. tetani*, and *Cl. botulinum* do not give active toxins, whereas *Cl. œdematiens*, *Cl. sordellii*, *Cl. chauvœi*, *Cl. sporogenes*, *Cl. centrosporogenes*, *Cl. tertium*, and *Cl. bifermentans* produce more or less reaction. The reactions were inhibited only by the homologous antisera. *Pseudomonas pyocyanea* also gave a reaction with lecitho-vitellin, which was inhibited by *Cl. welchii* antitoxin. W. E. van Heyningen [79] and E. F. Gale and W. E. van Heyningen [80] have described the preparation and partial purification of the α-toxin of *Cl. welchii*.

Complement.

In a series of papers Ecker and Pillemer and their co-workers [81–93] have described the preparation and properties of the various components of complement and elucidated their rôle in the process of specific complement fixation. To summarise briefly, they found that at 1° components C1 (mid-piece, insoluble in CO_2; may contain also C3 and C4), C2 (end-piece, soluble in CO_2; may contain also C3 and C4) and C4 (fourth component, inactivated by ammonia) combine with sensitised sheep red blood corpuscles, but C3

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[76] *J. Path. Bact.*, 1941, **52**, 99.
[77] *Biochem. J.*, 1941, **35**, 884.
[78] *Brit. J. Exp. Path.*, 1942, **23**, 37.
[79] *Biochem. J.*, 1941, **35**, 1246, 1257.
[80] *Ibid.*, 1942, **36**, 624.
[81] E. E. Ecker, L. Pillemer, C. B. Jones, and S. Seifter, *J. Biol. Chem.*, 1940, **135**, 347.
[82] E. E. Ecker, L. Pillemer, and A. O. Kuehn, *Proc. Soc. Exp. Biol. Med.*, 1940, **45**, 115.
[83] L. Pillemer, S. Seifter, and E. E. Ecker, *ibid.*, p. 130.
[84] L. Pillemer and E. E. Ecker, *J. Biol. Chem.*, 1941, **137**, 139.
[85] *Idem, Science*, 1941, **94**, 437.
[86] E. E. Ecker and L. Pillemer, *J. Immun.*, 1941, **40**, 73.
[87] E. E. Ecker, C. B. Jones, and A. O. Kuehn, *ibid.*, p. 81.
[88] L. Pillemer, S. Seifter, and E. E. Ecker, *ibid.*, pp. 89, 97.
[89] L. Pillemer and E. E. Ecker, *ibid.*, p. 101.
[90] L. Pillemer, E. E. Ecker, J. L. Oncley, and E. J. Cohn, *J. Exp. Med.*, 1941, **74**, 297.
[91] L. Pillemer, S. Seifter, and E. E. Ecker, *ibid.*, 1942, **75**, 421.
[92] L. Pillemer, S. Seifter, F. Chu, and E. E. Ecker, *ibid.*, 1942, **76**, 93.
[93] L. Pillemer, F. Chu, S. Seifter and E. E. Ecker, *J. Immun.*, 1942, **45**, 51.

(third component, inactivated by zymin or by an insoluble carbohydrate from yeast [84]) does not. C1, although combining with sensitised cells in the absence of C4, is hæmolytically inert unless C4 combines previously or simultaneously. C4 does not combine in the absence of C1. Although C3 is not fixed by antibody-red-cell aggregates, it is essential for hæmolysis, acting on the sensitised cells after fixation of C1, C2 and C4 and behaving as though it were a catalyst or enzyme.

M. Heidelberger [94] developed a method of estimating the amount of complement fixed by antigen–antibody complexes, which was used by Pillemer and co-workers [93] to estimate the amounts of the various components fixed.

J. Gordon and W. R. Atkin [95] showed that the inhibition of complement action by sodium hexametaphosphate (calgon) was due to combination with serum protein and not to removal of calcium.

C. G. A.

3. Proteolytic Enzymes.

Recent advance in our understanding of proteolytic enzymes has depended primarily on the work of the Northrop school,[1] who purified and crystallised the protein-digesting enzymes of the stomach and pancreas. Pepsin, trypsin, chymotrypsin and their inactive precursors have all been prepared in this way, usually from more than one species (pig, ox, sheep, chicken, and salmon [2]), and a beginning made in the study of pepsin as regards chemical composition, the nature of the groups connected with their activities, and the changes which occur when the inactive zymogen is converted autocatalytically into active pepsin. The other enzymes, like the more recently crystallised pancreatic carboxypeptidase of M. L. Anson,[3] have so far received scant chemical attention, and little work has been done on species differences in composition, though it has been shown that swine and salmon pepsin have different tyrosine contents.[1, 2] The position is complicated by the recent discovery [4] that crystalline swine pepsin, originally believed homogeneous, can be fractionated into at least two components of different proteolytic activity.

Enquiries into the presence of any non-protein prosthetic group particularly responsible for the enzymatic activity have so far yielded negative results : this stands in contrast to work on intestinal peptidases, which when partially purified are found to require manganous, cobalt, zinc or magnesium ions for activation.[5] In the case of pepsin, the early work of R. Herriott and J. H. Northrop,[1] studying the effect of acetylation with keten, and iodination, on the activity, pointed to the phenolic hydroxyl of the tyrosine residues (of which there is 12% in mammalian pepsin), together with the many free carboxyl groups of the protein, as primarily responsible. J. St. C. Philpot and A. Small,[6] investigating the iodination of tyrosine in more detail, later claimed that some unknown reactive group must be present, since iodination and inactivation proceed faster than the decrease in reactivity with Folin phenol reagent, which marks the formation of di-iodotyrosyl groups. Recently, R. M. Herriott [7] showed that this result was due to the intermediate formation of monoiodotyrosine, which has a stronger reaction with the Folin reagent than tyrosine itself.

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[94] *Science*, 1940, **92**, 534.

[95] *Brit. J. Exp. Path.*, 1941, **22**, 226.

[1] J. H. Northrop, " Crystalline Enzymes," Columbia University Press, 1937.

[2] E. R. Norris and D. W. Elam, *J. Biol. Chem.*, 1940, **134**, 443.

[3] *Ergebn. Enzymforsch.*, 1938, **7**, 118.

[4] R. Herriott, V. Desreux, and J. H. Northrop, *J. Gen. Physiol.*, 1939, **23**, 439; 1940, **24**, 213.

[5] Review by M. J. Johnson and J. Berger, *Advances in Enzymology*, 1942, **2**, 69.

The specificity of these enzymes has been investigated by Bergmann and his collaborators, using a wider range of synthetic substrates than previously available, prepared by his own carbobenzyloxy-method.[8] He began by showing that, like the peptidases, the proteinases also would attack simple peptides, but always provided that the terminal amino- and/or carboxyl groups of the peptide chain were blocked. Trypsin, for example, splits benzoylglycyl-lysineamide, but not glycinelysineamide or benzoylglycyllysine; pepsin splits carbobenzyloxyglutamyltyrosine but not glutamyltyrosine. Bergmann has explained this in terms of the undesirability of a positive or negative charge on the substrate close to the link to be broken, but it must be noted that carbobenzyloxylation introduces another peptide bond, and it seems possible that the enzyme requires at least one other peptide bond to combine with its substrate, in addition to that actually broken. This is made probable by the fact that pepsin also splits glycylglutamyltyrosine at a reasonable rate. Conversion of the carboxyl groups into amide makes the substrate resistant to peptic hydrolysis, but the conclusion that a negative (carboxylate ion) charge adjacent to the attacked link is essential is unwarranted, since carbobenzyloxyglutamyltyrosylglycine is also split, though rather more slowly. On the other hand, iodination of the tyrosine, and probably conversion of the γ-carboxyl into amide, makes the substrate completely resistant to pepsin. If tyrosine is replaced by phenylalanine in the peptide, the bond is still broken, but the rate is slower, which may mean that the enzyme substrate affinity is smaller.[9] Tryptophan-containing peptides have not been studied.

In a similar way, alterations in the typical substrates for other enzymes change their digestibility. Trypsin, for example, does not attack benzoylglycyl-lysineamide if the ε-amino-group of the lysine is carbobenzyloxylated: quite apart from charge effects, steric factors may also enter here. That spatial disposition is important is shown by the fact that if any of the amino-acids in the peptide are not of the lævo-configuration, the peptide becomes resistant to attack. Bergmann [10] explains this as meaning that the enzyme must actually attach itself to the peptide bond under attack, and the fact that methylation of the imino-group of the bond again prevents its breakage perhaps offers some support for this concept.

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[6] *Proc. Roy. Soc.*, 1939, *A*, **170**, 62. [7] *J. Gen. Physiol.*, 1941, **25**, 185.

[8] Reviews by M. Bergmann, *Advances in Enzymology*, 1941, **1**, 63; 1942, **2**, 49.

[9] J. S. Fruton and M. Bergmann, *J. Biol. Chem.*, 1939, **127**, 627.

[10] M. Bergmann *et al.*, *ibid.*, 1935, **109**, 325; 1937, **117**, 189.

Proteinases, then, attack even so small a protein fragment as a tripeptide, provided it contains the particular amino-acids to which the proteinase is adapted: pepsin must have an aromatic, and preferably a dicarboxylic amino-acid adjacent; chymotrypsin, a pancreatic enzyme with optimum pH 7·6, also demands an aromatic amino-acid component, but splits the bond on the other side of it, *i.e.*, bond 2 in

Carbobenzyloxyglutamyl|^{1}tyrosyl|^{2}glycineamide

where pepsin splits bond 1 of the same substrate.[11] This specificity is to some extent bound up with the charge character of the substrate, and this helps to explain the existence of a pH optimum. The fact that the optimum for pepsin with protein is in the neighbourhood of 2·5 may perhaps be reconciled with the value of 4·1 obtained with synthetic substrates by a difference of surface pH and bulk pH.[12]

With the knowledge gained from the study of pure enzymes, the Bergmann school have turned to the investigation of the enzyme mixtures of papaya latex, and later, with marked success, to the intracellular proteinases and peptidases of spleen and kidney. By comparing the activity towards various synthetic substrates of preparations after various activation treatments, with cyanide, hydrogen sulphide, etc., it has been possible to identify in beef spleen, a pepsinase, a trypsinase, a carboxypeptidase, and a leucine aminopeptidase, which are different from, but similar in hydrolytic specificity to, the digestive enzymes after which they are named, and to the similar enzymes present in kidney of ox and pig.[13] On the basis of results obtained with papain preparations, two of which have been in crystalline form,[14] Bergmann has proposed that these intracellular proteinases, formerly collectively termed cathepsin, play a synthetic rôle *in vivo*. He finds that glycyl-leucine is not attacked by cystine-activated papain, unless acetylphenylalanylglycine is simultaneously present, as a " co-substrate." The sequence of reactions is first synthesis of acetylphenylalanyl-glycyl-leucine; from this leucine is split off, then glycine is liberated, and so the co-substrate is regenerated and the peptide split. This means that an enzyme will not display its true specificity in presence of a peptide mixture, for example, a partial protein hydrolysate, and also shows that synthesis, like hydrolysis, is specific and dependent on the peptide mixture with which the enzyme has to deal: it suggests in fact a way in which foreign proteins (viruses, antigens) may deflect the normal course of protein synthesis. It should be noted in this connection that the equilibrium of these enzymatic reactions is very far on the side of hydrolysis, so that unless the product is removed from the system, or energy is supplied in some as yet unknown way, any measurable degree of synthesis of peptides by these proteinases is exceedingly improbable.

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[11] M. Bergmann and J. S. Fruton, *ibid.*, 1937, **118**, 405.

[12] G. S. Hartley and J. W. Roe, *Trans. Faraday Soc.*, 1940, **36**, 105; J. L. Danielli, *Biochem. J.*, 1941, **35**, 470.

[13] See *Advances in Enzymology*, 1942, **2**, 57.

[14] A. K. Balls and H. Lineweaver, *J. Biol. Chem.*, 1939, **130**, 669.

In the short space available it has been impossible to include any separate discussion of peptidases (see ref. 5), which in any case are still in a more undeveloped state, nor can we do more here than refer to the meagre physicochemical work as yet done on proteolytic enzymes.[15]

J. L. C.
A. N

4. Some Plant Products and Enzymes.

Owing to wartime preoccupations the output of published papers shows a continued decline; nevertheless, although there appears to be no outstanding achievement during the year under review, a steady advance is being maintained. The subjects dealt with in this Section are similar to those in previous years. The problem of starch is still engaging the attention of many workers; knowledge of growth factors for both higher and lower plants accumulates; improvements in the technique of protein investigation continue to be made.

Of reviews on the subject of the chemistry of plant products which have appeared recently, two may be mentioned here. A review of the lipoid constituents of algæ, with special reference to the carotenoids and sterols, is given by I. M. Heilbron,[1] and an account of recent progress in the chemistry of pectic materials and plant gums is contributed by E. L. Hirst.[2] It may also be mentioned that an account of polysaccharides, particularly in their structural aspects, was given by S. Peat in last year's *Annual Report*.[3] Some of the subject matter of the review by Hirst and the Report by Peat is again referred to briefly in this Report in order to maintain some slight degree of continuity.

Growth Substances.—The close association of auxin with leaf proteins is indicated by experiments of S. G. Wildman and S. A. Gordon,[4] who have isolated the leaf proteins of spinach and obtained from them by the action of proteolytic enzymes a separation of auxin. The most active enzyme in this respect was the mixture contained in a commercial tryptic extract, but other proteolytic enzymes were also effective, including trypsin and papain. Auxin was obtained in this manner from both cytoplasmic and chloroplastic proteins, and in the former case two fractions of protein were prepared by an isoelectric method, auxin being obtained from each fraction, but in differing amounts. The authors concluded from diffusion rates that the leaf auxin had a lower molecular weight than indolylacetic acid.

Wide variations in the auxin content of some algæ were discovered by J. van Overbeek.[5] The auxin present appears to be indolylacetic acid or one of its homologues; auxin-a or -b was apparently not present. The highest auxin concentration was found in the young blades. The same author has studied the occurrence of auxin and its precursor in coleoptiles of *Zea* and

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[15] J. A. V. Butler, *J. Amer. Chem. Soc.*, 1941, **63**, 2968, 2971.

[1] *J.*, 1942, 79.

[2] *Ibid.*, p. 70.

[3] *Ann. Reports*, 1941, **38**, 150.

[4] *Proc. Nat. Acad. Sci.*, 1942, **28**, 217.

[5] *Plant Physiol.*, 1940, **15**, 291.

Avena seedlings.[6] He finds that larger amounts of auxin can be removed from the coleoptile tips, wherein it is formed, by diffusion into agar than by ether extraction. After all the auxin obtainable by diffusion has passed out, there still remains a residue extractable by ether. A differentiation is made between "active" auxin extractable by ether, and "potential" auxin, obtained by diffusion plus that obtained by ether extraction, and the difference between these two represents the auxin precursor. It is considered that the temporarily delayed growth observable on decapitation of the growing tip is due not to lack of precursor of the auxin, but to lack of activation of such precursor. This activation occurs at the apical surface and is delayed by damage to the apical cells.

A new method of preparation of pure biotin has been described by D. B. Melville, K. Hofmann, E. Hague, and V. du Vigneaud,[7] who employ a biotin concentrate prepared commercially from milk. The crude biotin obtained from this source was purified by chromatographic adsorption applied to the methyl ester, the adsorbents employed being Decalso and activated alumina. From the purified methyl ester, the crystalline biotin was obtained after saponification. The method should be applicable to the preparation of relatively large amounts of biotin. Additional proof that biotin is a cyclic urea derivative is adduced by D. B. Melville, K. Hofmann, and V. du Vigneaud,[8, 9] who find that the diamino-carboxylic acid $C_9H_{18}O_2N_2S$ prepared from biotin is reconverted into biotin by the action of carbonyl chloride. In a further contribution to the study of the structure of biotin, the same authors [10] describe a number of derivatives of biotin and suggest several possible structures; but finality has not been reached.

A microbiological method for assay of biotin is described by G. M. Schull, B. L. Hutchings, and W. H. Peterson.[11] The organism employed is *Lactobacillus casei* ε and the method utilises the principle that under properly standardised conditions the titratable acidity produced by the organism is a function of the quantity of biotin present in the medium. Advantages claimed for the method are that it is independent of the effects of colour or turbidity in the solutions employed, that its accuracy is within 10%, and that, since the same organism is employed for assay of pantothenic acid [12] and riboflavin,[13] it is not necessary to maintain separate stock cultures. The biotin contents of a number of widely differing animal and plant sources have been determined by the method, and the results tabulated.

Further information is now available with regard to the nature of an antibiotin factor first noticed by R. E. Eakin, E. E. Snell, and R. J. Williams,[14, 15] who named their material avidin. This substance occurs in egg-white, and active concentrates were prepared and shown to combine stoicheiometrically with biotin, rendering it unavailable to yeast. D. W. Wooley and L. G. Longsworth [16] had also noticed that egg-white rendered biotin ineffective for *Clostridium butylicum*, and commenced work on the concentration and attempted isolation of the substance responsible. The work of the last-named confirms that of Eakin *et al.* and extends the latter's observations. They were able to prepare a substance from egg-white which was 15,000 times more effective against biotin than the original egg-white. This product appears to be a basic protein of isoelectric point pH 10; it was not obviously crystalline but was homogeneous under electrophoresis and in the ultra-centrifuge. It is concluded that it is a pure substance and a molecular weight of 70,000 is ascribed to it, although the true figure may be slightly lower.

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[6] *Amer. J. Bot.*, 1941, **28**, 1.

[7] *J. Biol. Chem.*, 1942, **142**, 615.

[8] *Science*, 1941, **94**, 308.

[9] *Ann. Reports*, 1941, **38**, 250.

[10] *J. Amer. Chem. Soc.*, 1942, **64**, 188.

[11] *J. Biol. Chem.*, 1942, **142**, 913

[12] D. Pennington, E. E. Snell, and R. J. Williams, *ibid.*, 1940, **135**, 213.

[13] E. E. Snell and F. M. Strong, *Ind. Eng. Chem.* (*Anal.*), 1939, **11**, 346.

[14] *J. Biol. Chem.*, 1940, **136**, 801.

[15] *Ibid.*, 1941, **140**, 535.

Additions to the group of bios substances may still be expected. Vitamin B_1 is generally recognised as a constituent necessary for many micro-organisms and vitamin B_6 also has been added to the list. C. Marchant [17] finds that *Saccharomyces hanseniaspora valbyensis* requires the known bios constituents, including vitamin B_6, which can be supplied in place of a " bios VII " solution.. In the case of *S. galactosus*, vitamin B_6 cannot replace the " bios VII " solution, and it is concluded that this must contain an additional unknown factor or factors.

In last year's Report[18] the use of *Proteus morganii* as an organism suitable for assay of pantothenic acid was described. In a more recent paper [19] an enquiry into the part played by pantothenic acid in the metabolism of the organism leads to the suggestion that the acid is concerned in some manner with the metabolism of pyruvic acid. The mechanisms involved are at present unknown, but the evidence largely points to the agency of pantothenic acid in converting pyruvic acid into acetic acid. It may be, however, that pantothenic acid is concerned in some other stage involving pyruvic acid or some intermediate derived from pyruvic acid.

In the search for analogues of pantothenic acid which might have biological acitivity of the kind associated with the acid, J. W. Barnett and F. A. Robinson [20] have prepared a number of products, including two new lactones, by condensing β-alanine with five different lactones, and by condensing α-hydroxy-ββ-dimethylbutyrolactone with four different amino-acids. None of the substances synthesised could replace pantothenic acid as a growth stimulator. It would seem that, if either the α-hydroxy-group is lost, or the carbon chain lengthened, the resulting product has no biological activity. On the other hand, the same authors found [21] that certain analogues of pantothenic acid had an inhibitory effect on *Streptococcus hæmolyticus* and *Corynebacterium diphtheriæ*. Such analogues were obtained by condensation of α-hydroxy-ββ-dimethylbutyrolactone with taurine and taurine amide and by condensation of β-hydroxy-γγ-dimethylvalerolactone and taurine. In these cases the inhibition was reversed by pantothenic acid; but with other analogues the inhibition was not reversible. In all the compounds dealt with in this manner, the α-hydroxy-group of pantothenic acid is absent.

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[16] *J. Biol. Chem.*, 1942, **142**, 285. [17] *Canadian J. Res.*, 1942, **20**, *B*, 21.

[18] *Ann. Reports*, 1941, **38**, 251.

[19] A Dorfman, S. Berkman, and S. A. Koser, *J. Biol. Chem.*, 1942, **142**, 393.

[20] *Biochem. J.*, 1942, **36**, 357. [21] *Ibid.*, p. 364.

Starch and Amylases.—Differences between the enzymically synthesised starch of C. S. Hanes,[22] and naturally occurring starch appear to be reflected in their constitutions. W. Z. Hassid and R. M. McCready [23] have approached the problem on recognised lines, and submitted the synthetic starch to methylation and hydrolysis. They were unable to isolate any tetramethyl glucose, the sole product appearing to consist of 2 : 3 : 6-trimethyl glucose. In the apparent absence of an end-group they suggest that the chains may exist as continuous loops of glucopyranose residues. It is possible, however, that the small quantity of synthetic starch available to these workers rendered the isolation of the small amount of tetramethyl glucose impossible, since an investigation of the enzymically synthesised starch by W. N. Haworth, R. L. Heath, and S. Peat [24] has shown that end-group assay is possible and that on methylation the starch gives a product, containing 44·5% of methoxyl, which resembles in general characters the product obtained similarly from potato starch, amylose, and amylopectin. They conclude that the unit chain-length is not less than 80—90 glucose units, the linkages being of the normal 1 : 4-α-glucosidic type. The length of this chain distinguishes the synthetic from the natural starch, and the length estimated in this manner agrees with that suggested by Hanes on the basis of copper-reducing power. The enzyme concerned in the production of synthetic starch, the phosphorylase of potato, has been examined and purified by D. E. Green and P. K. Stumpf,[25] who, by successive ammonium sulphate fractionations, have obtained a preparation some 370 times more concentrated than the original. They find that adenylic acid is not a component of the system, as is the case with animal phosphorylase, and that catalytic amounts of starch, dextrin or glycogen are required for starch formation from glucose 1-phosphate. No inhibition was observed when heavy metals, oxidising or reducing agents were present.

Although our knowledge of the structure of starch has been placed on a much firmer basis in recent years, none would suggest that the last word on the subject has yet been written. The presence of linkages other than the commonly accepted 1 : 4-glucosidic linkage is frequently suggested in the literature, and the problem is discussed by R. W. Kerr and N. F. Schink,[26] who have carried out experiments with particular reference to fermentability of syrups prepared by diastatic action on maize starch. In discussing structural problems, these authors stress especially the non-homogeneous nature of starch and claim the existence of at least two fundamentally different configurations in maize starch, probably only one of which is composed of the usual 1 : 4-glucoside or maltose type of linkage. A hint of other possible linkages is contained in the claim of Y. Nakamura [27] to have isolated a new disaccharide, " amylolyose," by the action of diastase on starch. The new sugar contains 1 : 5-linkages and it is suggested that, although the preponderant linkage between the glucose units in starch may be the normal 1 : 4 type, 1 : 5- and 1 : 3-linkages may also be present.

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[22] *Ann. Reports*, 1940, **37**, 419.

[23] *J. Amer. Chem. Soc.*, 1941, **63**, 2171.

[24] *J.*, 1942, 55.

[25] *J. Biol. Chem.*, 1942, **142**, 355.

[26] *Ind. Eng. Chem.*, 1941, **33**, 1418.

Increasing attention is being given to bacterial amylases, especially in their industrial aspects, and a comparison of the properties of a pure bacterial amylase and the α-amylase of malt is the subject of papers by R. H. Hopkins and D. Kulka [28] and R. H. Hopkins, D. E. Dolby, and E. G. Stopher.[29] It was found that the properties of the two amylases are very closely similar, although the bacterial enzyme is able to function at higher temperatures than the α-enzyme, and acts more powerfully, particularly in its ability to liquefy starch paste. The points of resemblance between the two enzymes are the rapidity of liquefaction of starch paste and the formation of dextrins, maltodextrin and a little maltose. This stage of the reaction is complete at about 35% of total hydrolysis in terms of maltose, after which reaction proceeds very slowly until it ceases at about 90% of total hydrolysis. Very varying dextrins are produced in the first stage of the reaction, the maltodextrin obtained having R 33 (maltose, R = 100), and another dextrin formed having R 15 or less.

The well-known production of the non-reducing, crystalline dextrins from starch under the action of *Bacillus macerans* affords another example of bacterial amylase action, and the enzyme has been the subject of recent studies by E. B. Tilden, M. Adams, and C. S. Hudson.[30, 31] By an elaborate method of purification, involving adsorption on alumina and subsequent elution with phosphate, an enzyme preparation has been obtained which is some 140 times as active as the original. The crystalline dextrins themselves have been the object of study by D. French and R. E. Rundle,[32] who have determined the molecular weights of the Schardinger α- and β-dextrins of potato starch. *X*-Ray diffraction experiments, combined with crystal density measurements, led the authors to the conclusion that in the first case there were six glucose units in the molecule, and in the latter seven.

Hemicelluloses, etc.—The outstanding difficulties in the isolation of hemicelluloses still remain those of pre-treatment of material, and subsequent extraction. The products obtained are almost invariably mixtures resulting from varying degrees of attack on the encrusting hemicelluloses themselves and on the cellulose fraction. The subject is again discussed by I. A. Preece,[33] who confirms the loss of hemicellulose material resulting from pre-treatment with boiling alkali. Hot alkaline extraction favours the dissolution of non-pentosan, whereas cold extraction favours the dissolution of xylan. The relative proportions of these types in the mixture obtained vary with the raw material and the conditions of its treatment.

Hemicelluloses conforming to the general type of those found in hardwoods have been isolated by E. Anderson, R. B. Kaster, and M. G. Seeley [34] from cotton-wood, *Populus Macdougali.* They comprise a mixture of molecules of a methoxyuronic acid combined with a chain of xylan units. The chain in this case appears to be smaller than is usually the case, consisting as it does of only 7—9 xylan units. The presence of starch was indicated by the iodine coloration in the hemicelluloses extracted prior to chlorination, but it was absent from the products obtained after chlorination. It is suggested that the composition of these hemicelluloses indicates a possible origin by partial oxidation or decarboxylation of starch or dextrin. The presence of pectic substances in the wood was confirmed by isolation of a product probably identical with pectic acid. Another wood product, an arabogalactan of larch, is described and discussed by E. V. White.[35, 36] Similar fractions of the product are obtained by water extraction of the sawdust, and subsequent precipitation with alcohol. A study of the products of acetylation and methylation leads to the conclusion that the polysaccharide consists of a highly branched chain of galactose units. Terminal groups of arabofuranose and galactopyranose are attached to carbon atom 6 of the units of the galactose chain.

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[27] *J. Agric. Chem. Soc. Japan*, 1941, **17**, 779.

[28] *J. Inst. Brew.*, 1942, **48**, 170.

[29] *Ibid.*, p. 174.

[30] *J. Bact.*, 1942, **43**, 527.

[31] *J. Amer. Chem. Soc.*, 1942, **64**, 1432.

[32] *J. Amer. Chem. Soc.*, 1942, **64**, 1651.

[33] *Biochem. J.*, 1941, **35**, 659.

In addition to starch, which comprises the bulk of the seed, oat seeds have been shown to contain lævans, and amongst other possible polysaccharides, D. L. Morris [37] has isolated and examined lichenin and an araban. The author revives the hypothesis of Karrer that lichenin may be widespread in nature as a " reserve cellulose," and shows that this is the polysaccharide responsible for the cupric chloride crystallisation pattern. These crystal patterns are not without interest. It was shown by D. L. Morris and C. T. Morris [38] that the crystal form of cupric chloride was unaffected by inorganic salts, simple sugars and glycine, but that solutions of polysaccharides such as starch and glycogen produced patterns which were characteristic of the added substance. A substance in oats gave a characteristic pattern, shown above to be due to lichenin. Cupric chloride crystal patterns were employed by the authors [39] in the identification of a carbohydrate in *Zea mays* shown to be glycogen, athough it was noticed that some substance appeared to be present which rendered the patterns for the *Zea* extracts slightly different from those of other samples of glycogen. The isolated glycogen gave patterns identical with those for animal glycogen. The substance responsible for the differences in the extracts was found [40] to be a protein or proteins, and the effect of the protein appears to be dependent on the total amount of protein present rather than on the ratio of protein to polysaccharide. The specificity of the patterns is due to the polysaccharide and the action of the protein is entirely non-specific.

Other polysaccharides recently investigated include an insoluble polysaccharide of yeast, the mucilage of the seed of Indian wheat, and a new rhamnosan. The structure of the first of these, the so-called yeast cellulose, has been investigated by W. Z. Hassid, M. A. Joslyn, and R. M. McCready,[41] who confirm the findings of L. Zechmeister and G. Toth,[42] that the glucosidic linkages in the molecule are of an unusual character. After methylation and hydrolysis the sole product was 2 : 4 : 6-trimethyl glucose ; no trace of tetramethyl glucose could be found, and hence it follows that the molecule consists most probably of a closed chain whose glucopyranose units are combined through carbon atoms 1 and 3, and not 1 and 4 as is most generally the case. Evidence was also adduced to show that the glucosidic linkages were predominantly of the β-type, and viscosity measurements indicated a molecular weight of about 6500. The mucilage of the seed of Indian Wheat, a native of the arid regions of the south-western United States, is similar in composition to that of Psyllium seed,[43] and was obtained in about 19% yield. On the basis of hydrolysis and isolation of the sugars formed, and of determination of pentosan and uronic acid, E. Anderson, L. A. Gillette, and M. G. Seeley [44] conclude that the mucilage consists of aldobionic acids containing galacturonic acid and arabinose, combined with xylose, and a small fraction which resists solution on hydrolysis. More precise evidence of structure can only be established by further examination. A preliminary note on a new rhamnose-containing polysaccharide from one of the Chlorophyceæ, *Ulva lactuca*, is contributed by M. M. T. Plant and E. D. Johnson.[45] It is weakly acidic and non-reducing, and, like other algal polysaccharides, it contains a sulphuric ester grouping, but, unlike some others of this type, it does not contain uronic acid residues. Rhamnose was identified as a product of hydrolysis and further examination of the polysaccharide is to be undertaken.

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[34] *J. Biol. Chem.*, 1942, **144**, 767.

[35] *J. Amer. Chem. Soc.*, 1941, **63**, 2871.

[36] *Ibid.*, 1942, **64**, 302.

[37] *J. Biol. Chem.*, 1942, **142**, 881.

[38] *J. Physical Chem.*, 1939, **43**, 623.

[39] *J. Biol. Chem.*, 1939, **130**, 535.

[40] *Ibid.*, 1941, **141**, 515.

Proteins and Amino-acids.—A crystalline protein preparation of somewhat unusual properties is described by A. K. Balls,[46] and by this author with W. S. Hale and T. H. Harris.[47] It was derived from a light petroleum extract of flour, and was precipitated therefrom, after removal of sterols, by ether and alcoholic hydrochloric acid. It could be crystallised from 75% alcohol, and examination showed it probably to be the hydrochloride of an oxidised fragment of a lipo-protein, containing cysteine, in the original flour. The chief amino-acids present, to about two-thirds of the total, were arginine, cystine and tyrosine. It was found to be toxic to yeasts and to some animals ; it reversibly inhibits chymopapain and protects carotene from oxidation by carotene oxidase. It is attacked by proteolytic enzymes such as trypsin.

The effect of the conditions of hydrolysis of zein on the products obtained has been examined by R. Borchers and C. P. Berg,[48] since it had been observed that zein hydrolysates obtained by sulphuric acid hydrolysis in the autoclave at 165° gave anomalous results in growth experiments with young rats. It was thought that racemisation or destruction of essential constituents might have occurred under the conditions of hydrolysis, since the optical rotation of the hydrolysate under autoclaving was lower than that obtained by refluxing. Using acid of concentration between 14 and 33% by volume in a series of experiments it was found that no racemisation or destruction occurred either in refluxing or in autoclaving at 120—180°. The refluxing could be considerably prolonged with little or no harmful effect, but continuation under the autoclave beyond the time necessary for hydrolysis induced both racemisation and destruction. It was considered that sulphuric acid of as low a concentration as 8% was unsuitable for complete and satisfactory hydrolysis of zein.

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[41] *J. Amer. Chem. Soc.*, 1941, **63**, 295.

[42] *Biochem. Z.*, 1934, **270**, 309; 1936, **284**, 133.

[43] E. Anderson and M. Fireman, *J. Biol. Chem.*, 1935, **109**, 437.

[44] *Ibid.*, 1941, **140**, 569.

[45] *Nature*, 1941, **147**, 390.

[46] *J. Washington Acad. Sci.*, 1942, **32**, 132.

[47] *Cereal Chem.*, 1942, **19**, 279.

[48] *J. Biol. Chem.*, 1942, **142**, 693.

In a further communication, R. Borchers, J. R. Totter, and C. P. Berg [49] have traced the failure of autoclave hydrolysates of zein to support growth of rats on otherwise suitable diets, in part, at least, to the loss of threonine, whose structure renders it specially liable to racemisation. The loss of threonine is not great under reflux or mild autoclave treatment in hydrolysis, but becomes increasingly marked as autoclave conditions become more drastic.

A brief discussion of some of the methods now being employed in the isolation of protein hydrolysis products was included in last year's *Annual Report*,[50] and to these may be added investigations by R. L. M. Synge and co-workers. The investigations had as their object the examination of hydrolysates from animal proteins, but inasmuch as the methods are of general application, and in part involve new physico-chemical applications, they may be included here. In a series of papers published in 1939, R. L. M. Synge [51] describes experiments to determine the partition coefficients of a number of acetamido-acids between immiscible solvents, notably chloroform and water, and also ether and ethyl acetate–water systems. The preparation of a number of acetamido-acids is described, including some not previously prepared. If such technique is to be of service in separating amino-acids from the mixture in an hydrolysate, it would be necessary to acetylate the amino-acids of the hydrolysate and to obtain the acetyl compounds in pure form. Separation on the basis of their different partition coefficients between chloroform and water would follow. A known mixture of amino-acids being used, it was shown that those susceptible to fractional extraction in this way were recovered in high yield. The acetylhydroxy-amino-acids are almost entirely extracted from aqueous solution by chloroform. A means of isolation of these acids was sought *via* the acetylbenzoyl derivatives. A method for preparing the serine and hydroxyproline derivative was evolved, and it was found that such derivatives were debenzoylated by alkali at room temperature and deacetylated by boiling dilute acid. On the basis of these properties a method of isolation of the hydroxyamino-acids in protein hydrolysates was worked out. In the last paper of this particular series the methyl esters of the acetylhydroxyamino-acids were prepared, their partition between water and chloroform measured, and the results applied to the separation of hydroxyamino-acids in protein hydrolysates. In a later communication by A. J. P. Martin and R. L. M. Synge [52] the extractional fractionation of amino-acids in protein hydrolysates as acetyl derivatives is carried a considerable step forward. The design, construction and operation of a 40-unit counter-current liquid-liquid extraction apparatus is described, and by its means a satisfactory procedure for the isolation and determination of methionine, valine, proline, leucine and phenylalanine was elaborated. On test with known mixtures of the amino-acids the results showed that the method had some advantages over Dakin's butyl alcohol extraction, followed by Fischer's ester distillation.

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[49] *J. Boil. Chem.*, 1942, **142**, 697.
[50] *Ann. Reports*, 1941, **38**, 256.
[51] *Biochem. J.*, 1939, **33**, 1913, 1918, 1924, 1931.

A renewed attack on the hydroxyamino-acid fraction is made by the same authors,[53] who studied next the applications of the reaction with periodic acid. Threonine yields acetaldehyde on treatment in neutral solution with periodate, and this may be removed by simple aeration. The other hydroxy-amino-acids do not yield acetaldehyde under these conditions, and the reaction is adapted to the purposes of a micro-determination of threonine. The other amino-acids yield formaldehyde under periodate treatment, but the determination of this by means of dimedone, for example, was unsatisfactory. It was found, however, that threonine and serine and periodate in presence of 50% potassium carbonate gave definite yields of ammonia, and this finding was applied to the determination of the amino-acids in complete protein hydrolysates. In further application of the acetylation–benzoylation technique previously mentioned, low recoveries of threonine in a wool hydrolysate were obtained; serine, however, was obtained in good yield. The same procedure applied to gelatin and isinglass yielded a substance similar to Van Slyke's hydroxylysine, which, like the latter, yielded form-aldehyde and ammonia with periodic acid. At a later date, A. J. P. Martin and R. L. M. Synge [54] have enlisted the aid of chromatography in the solution of the problem of the determination of the higher amino-acids in protein hydrolysates. A novel form of chromatogram is described, and a general theory of chromatography developed. The form employed depends not on adsorption on a solid phase but on partition of solutes between two liquid phases, and the visual detection of the colourless acids in the chromatogram is achieved by the use of an indicator added to one of the phases. The new chromatogram is successfully applied to a micro-determination of the amino-acids phenylalanine, leucine, proline, valine and methionine in artificial mixtures and in hydrolysates from wool.

Pigments.—In isolating the lipoid pigments from " Sherbro " palm oil, R. F. Hunter and A. D. Scott [55] consider that in the light of the physical properties, they have obtained purer specimens of α- and β-carotenes than any hitherto described in the literature. In addition to these they obtained γ-carotene, *neo*-γ-carotene, lycopene, *neo*lycopene and *neo*lutein. The chromatogram also revealed the presence of a new carotenoid adsorbed at a position intermediate between those of γ- and β-carotenes. The authors suggest that in the biogenesis of the carotenes, a common intermediate complex is the source of lycopene, β-carotene and γ-carotene, and that α-carotene may later arise from isomerisation of the β-compound. The carotenoid composition of the unsaponifiable matter of a West African plantation oil was shown by the same authors, with J. R. Edisbury,[56] to be qualitatively similar to that of the Sherbro oil, and again the new carotenoid intermediate on the chromatogram between γ- and β-carotene was observed. Ergosterol was also reported. In a discussion of the isomerisation of the carotenoids the authors draw an analogy between the reversible isomerisation of the carotenoids and the mobile *cis-trans* isomerism of azobenzene.

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[52] *Biochem. J.*, 1941, **35**, 91.

[53] *Ibid.*, p. 295.

[54] *Ibid.*, p. 1358.

[55] *Ibid.*, p. 31.

Although it has been established that some varieties of *Iris* owe their colour to members of the anthocyanin group, it was shown by van Wisselingh[57] and has recently been confirmed by W. F. O'Connor and P. J. Drumm [58] that the water-flag, *Iris pseudacorus*, owes its colour to carotenoids, of which β-carotene, violaxanthin and lutein have been isolated and characterised. There is evidence that zeaxanthin is present, and a red wax-like substance has also been noted. It is possible, on the evidence of adsorption bands in carbon disulphide solution, that this substance is closely identifiable with a similar substance observed by R. Kuhn and A. Winterstein [59] in the carotenoids of *Viola tricolor.*

The view has been very generally held that secondary products of plant metabolism once formed are then definitely eliminated from the metabolic processes of the plant. Examples are gradually accumulating, however, which indicate that some modification of this view is necessary, in particular where the normal metabolism of the plant is disturbed by etiolation. It has been found that when seedlings of *Salvia officinalis* are etiolated there is a resorption of essential oils.[60] Alkaloids have also been utilised by etiolated plants as shown in the cases of hordenine,[61] caffeine and theobromine,[62] and the alkaloids of *Lupinus luteus.*[63] Recent experiments by A. Frey-Wyssling and F. Blank [64] have shown that anthocyanins are utilised similarly. Seedlings of red radishes or red cabbage were found to develop anthocyanins very early on germination, but when the seedlings were subjected to the metabolic disturbances consequent on etiolation, the anthocyanins disappeared in a few days only at 95° F., and slowly during several weeks at 50° F.

The pigment present in some flowers, and notably the *Compositæ*, which gives an intense red coloration with alkali has been shown to be the chalkone butein. J. R. Price [65] has identified it in *Dahlia variabilis* and shown that it may be formulated as shown (I). It probably occurs both as such and as an easily hydrolysable glycoside. The pigment has also been isolated by T. A. Geissmann[66] from *Coreopsis Douglasii*, a native of Southern California, and in this case also it is evident that both glycoside and aglycone exist in the flower. The term anthochlor pigment is applied to this type of polyhydroxychalkone and others of the group are likely soon to be isolated. For instance, a pigment of *Coreopsis grandiflora* is under investigation and is probably a pentahydroxychalkone. The interest of these pigments lies not solely in their chemistry and structure, since they are equally important to the geneticist. Genetical data have shown that anthocyanins, flavones and pigments such as butein are derived from some common intermediate; increasing knowledge of the pigments derived from this intermediate will lead in turn to an understanding of the nature of the intermediate, and the stages in biogenesis of large groups of plant products may be revealed.

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[56] *Biochem. J.*, 1942, **36**, 697.

[57] *Flora*, 107, N.S. 7, 371.

[58] *Nature*, 1941, **147**, 58.

[59] *Ber.*, 1931, **64**, 332.

[60] A. Frey-Wyssling and F. Blank, *Verh. Schweiz. Naturf. Ges.*, 1940.

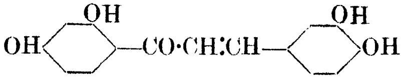
[61] Y. Raoul, *Compt. rend.*, 1937, **205**, 450.

[62] T. Weevers, *Arch. Néerl. Sci. naturelles*, 1930, **4**, 111/B.

[63] J. C. J. Wallebrook, *Rec. Trav. bot. Néerl.*, 1940, **37**.

[64] *Nature*, 1941, **147**, 148.

[65] *J.*, 1939, 1017.



(I.)

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[66] *J. Amer. Chem. Soc.*, 1941, **63**, 656.

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